wire 30–40 in. in length, while the cathode was a massive pool of metallic mercury. The reference electrode was an 8-in. length of bare silver wire isolated from the sample compartment by placing it in an immersion tube which contained the ethanolic solution of the electrolyte.

cis-2,*trans*-3-Diphenylcyclopropyl Chloride (1).—Into the electrolysis vessel was added a 0.13 *M* solution of tetraethylammonium bromide in 95% ethanol. A 1.0-g sample of 1,1-dichloro-*trans*-2,3-diphenylcyclopropane was added and the electrolysis was carried out at −1.65 to −2.0 V *vs.* the silver wire reference. When the current reading dropped to 1–2 mA, the electrolysis was stopped. The catholyte was removed and poured into water (500 ml), and the solution was refrigerated overnight. A white solid was obtained which was filtered, washed with water, and air dried to give 0.8 g (92%) of the monochlorocyclopropane, mp 62.5–63.5°. Recrystallization from 95% ethanol gave an analytical sample: mp 63–64°; uv max (95% C_2H_5OH) 222 nm (ε 19,440), 260 (697), 266 (681), and 273 (438); ir (KBr) 704 (s), 750 (s), 764 (s), and 1015 cm^{-1} (w); nmr (CCl_4) δ 2.61 (apparent d, 2), 3.40 (doublet of doublets, 1), and 7.0–7.28 ppm (m, 10).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.86; H, 5.78; Cl, 15.47.

cis-2,*cis*-3-Diphenylcyclopropyl Chloride (2).—The reduction of a 1.0-g sample of 1,1-dichloro-*cis*-2,3-diphenylcyclopropane was performed in the electrolysis cell. The solution of tetraethylammonium bromide in 95% ethanol was approximately 0.1 *M*. The reduction was carried out at −1.65 to −2.0 V *vs.* the silver wire reference. The catholyte was poured into 600 ml of water and refrigerated overnight. Filtration gave a solid material which was washed with water and air dried to afford 0.7 g (80%) of product. Recrystallization from 95% ethanol gave 0.5 g of colorless crystals, mp 69–71°. An analytical sample was obtained by vacuum sublimation: mp 71–72°; uv max (95% C_2H_5OH) 220 nm (shoulder, ε 13,690), 255 (433), 261 (473), 265 (shoulder, 392), and 272 (shoulder, 191); ir (KBr) 694 (s), 711 (vs), 728 (s), 778 (s), 788 (s), and 1030 cm^{-1} (w); nmr (CCl_4) δ 2.43 (d, J = 7.5 Hz, 2), 3.60 (t, J = 7.5 Hz, 1), and 6.8–7.17 ppm (m, 10).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.64; H, 5.86; Cl, 15.43.

trans-2,*trans*-3-Diphenylcyclopropyl Chloride (3).—A 0.7-g sample of 1,1-dichloro-*cis*-2,3-diphenylcyclopropane was reduced in the electrolysis vessel using absolute ethanol as the solvent at −1.65 to −1.9 V *vs.* the silver wire reference. The reaction period was about 2 hr. The catholyte was poured into water and extracted with ether. The ether layer was washed several times with water, dried ($MgSO_4$), and concentrated to a viscous oil consisting of a 1:3 mixture of 1-chloro-*trans*-2,*trans*-3-diphenylcyclopropane (3) and 1-chloro-*cis*-2,*cis*-3-diphenylcyclopropane (2) as determined by nmr.

Reduction of two 1-g samples of 1,1-dichloro-*cis*-2,3-diphenylcyclopropane in absolute ethanol followed by refrigeration of the oily mixtures gave, after filtration, 1.2 g of solid, mp 66–70°. On extraction of the filtrates with ether, 0.5 g of an oily material was obtained. Chromatography of the oil on neutral alumina, using low-boiling petroleum ether as the eluent, afforded about 0.1 g of liquid shown by nmr to be 1-chloro-*trans*-2,*trans*-3-diphenylcyclopropane: nmr (CCl_4) δ 2.81 (d, J = 4.5 Hz), 3.71 (t, J = 4.5 Hz), and 6.73–7.45 ppm (m).

Kinetics of 1 and 2.—A 0.020 *M* solution of the cyclopropyl chloride in acetic acid (0.040 *M* in sodium acetate) was prepared. Samples of 1.5–2.0 ml were sealed in ampoules and placed in the bath controlled to ±0.1°. The ampoules were removed and a 1-ml portion was diluted to 50 ml with 95% ethanol. A 1-ml portion of each initially diluted sample was further diluted with 9 ml of 95% ethanol and the absorbance was read at 253 nm. Since the cyclopropyl chlorides had a small absorbance at 253 nm, standard curves were necessary. Two infinity determinations were taken after 10 half-lives for each run.

Kinetics of Solvolysis of 3.—Since an isomerically pure sample of 1-chloro-*trans*-2,*trans*-3-diphenylcyclopropane was not practically obtainable, the solvolyses were performed using a mixture of 1-chloro-*cis*-2,*cis*-3- and 1-chloro-*trans*-2,*trans*,3-diphenylcyclopropane. A 0.014–0.040-g sample was dissolved in 2 ml of acetic acid (0.040 *M* in sodium acetate). About 1.0–1.5 ml of the solution was injected into a 2-ml vial capped with a rubber septum. A 50-μl Hamilton syringe was used to remove samples. At the start of a run, two 30-μl portions of the solvolysis mixture were diluted to 25 ml with 95% ethanol and the absorbance was read at 253 nm. Samples of 30 μl were removed at appropriate intervals, diluted, and read. Several infinity determinations were taken after 8 half-lives for each run.

Registry No.—1, 36611-95-7; 2, 36611-96-8; 3, 36611-97-9; 1,1-dichloro-*cis*-2,3-diphenylcyclopropane, 36611-98-0.

Acknowledgment.—This work was supported in part by the National Aeronautics and Space Administration.

Methylation of α-Chloro Ketones *via* Halohydrin Formation and Rearrangement

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A new procedure for the stereoselective introduction of an angular methyl group in two systems (1-decalone and perhydro-1-indanone) is outlined. Two monocyclic systems, cyclohexanone and 2-methylcyclohexanone, were also methylated. The sequence of reactions by which the angular methyl group was stereoselectively introduced entailed the following: the preparation of the α-chloro ketone with sulfuryl chloride, followed by its conversion to the halohydrin with methyllithium, and, lastly, transformation to the magnesium salt of the halohydrin (isopropylmagnesium bromide) followed by decomposition resulting in the production of the methylated ketone. The reaction is discussed from the synthetic and mechanistic viewpoints. The noteworthy disadvantage of the sequence is that the *trans*-methyl (angular methyl) isomers cannot be prepared; *only* the pure cis isomers can be obtained.

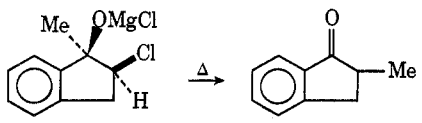
One of the more intriguing, challenging and seemingly endless areas of research in organic chemistry involves uncovering diverse approaches for the introduction of an angular methyl group into steroids and steroid-like systems. Still more challenging is to effect the *stereoselective* introduction of the angular methyl group into the system. To recount all the many excellent and efficacious methods and ingenious assaults at the problem is beyond the purpose and scope of this manuscript; suffice to mention some salient and excellent leading references.[2]

The rearrangement of the magnesium salts of halohydrins to ketones has long been known and its application to the synthesis of α-alkyl- and α-aryl-sub-

(1) From the Ph.D. Dissertation of A. C. Vitale, Adelphi University, 1970.

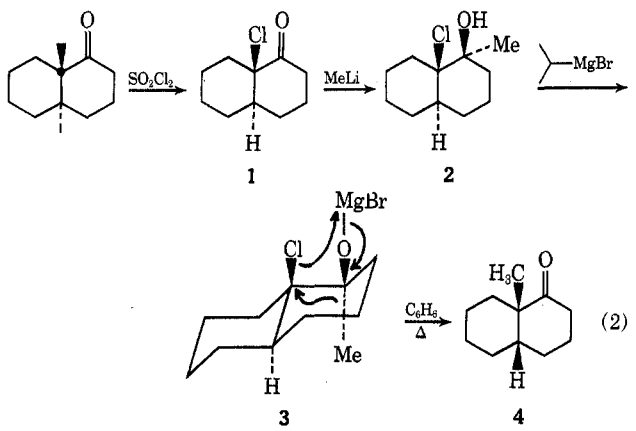
(2) R. P. Linstead, *Annu. Rep. Chem. Soc.*, **33**, 312 (1936); H. D. Springall, *ibid.*, **36**, 286 (1939); H. Wynberg, *Chem. Rev.*, **60**, 178 (1960); R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962); R. E. Ireland, D. R. Marshall, and J. W. Tilley, *J. Amer. Chem. Soc.*, **92**, 4754 (1970).

stituted ketones has also been well established.[3] More recently[4] the reaction was applied to effect various ring enlargements and it has offered a simple, new procedure. Geissman and Akawie[3] extensively studied the reaction producing ketones *via* the decomposition of the magnesium salts of halohydrins and observed that primary halides do not rearrange unless a good migrating group is involved and that secondary and tertiary halides do undergo reaction independent of the nature of the migrating group. More importantly, their stereochemical studies convincingly demonstrated that the halo and hydroxyl groups must be cis (or must attain the cis alignment in nonrigid systems) to effect the rearrangement. The trans isomer leads to extensive decomposition. Thus the results preclude an epoxide rationale for the rearrangement and leave as plausible a pinacol-type mechanism with the magnesium atom functioning as the electrophile (eq 1). In a preliminary



(1)

communication[5] the first application of the aforementioned reaction to a *stereoselective* introduction of an angular methyl group into *trans*-1-decalone was described. The sequence entailed the treatment of *trans*-1-decalone with sulfuryl chloride to yield a mixture of *cis*- and *trans*-9-chloro-1-decalone from which by a previously described procedure[6] *trans*-9-chloro-1-decalone (**1**) was isolated (10% yield). The compound **1** was then treated with methyllithium, whose expected approach to the carbonyl carbon from the least hindered side (opposite the chloro group) should produce the halohydrin **2** with the prescribed geometry necessary for the rearrangement (chloro and hydroxyl groups cis) (eq 2). Finally, the conversion of the crude halo-



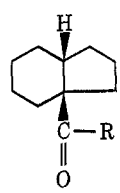
(2)

hydrin **2** to its magnesium salt **3** followed by its decomposition in refluxing benzene solution produced *only* *cis*-9-methyl-1-decalone (**4**) (58% yield based on **1**).

This manuscript presents the results of further studies of the rearrangement with the decalone system and with other simple systems.

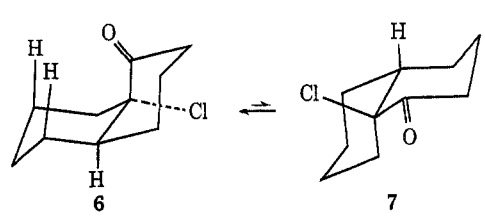
A procedural improvisation for the production of **4** entailed the direct decomposition of the intermediate lithium salt of the halohydrin **2**. The latter thus avoids the additional effort and time involved in the isolation of the halohydrin **2** and its subsequent conversion to the magnesium salt as previously reported.[5] Undoubtedly, the success of the reaction can be attributed to the known fact that the lithium ion possesses a coordination number of four,[7] thereby rendering it with electrophilic properties similar to those of the magnesium ion (coordination number four also).

Many varied attempts to separate the *cis*- from the *trans*-9-chloro-1-decalone were fruitless. Others similarly reported that their efforts were unrewarded.[6] However, after the removal of some of the pure **1** by fractional crystallization the residue composition, after its distillation, consists of approximately equal amounts of the cis and trans isomers.[6] It was therefore decided to ascertain the product(s) of the rearrangement from the *cis*-9-chloro-1-decalone utilizing the mixture of stereoisomers. Accordingly, the mixture of *cis*- and *trans*-9-chloro-1-decalone was treated with methyllithium, resulting in a stereoisomeric mixture of halohydrins which was subsequently converted to the magnesium salt with isopropylmagnesium bromide. The latter was decomposed in refluxing benzene to yield the expected **4** and methyl *cis*-hexahydroindan-3*a*-yl ketone (**5a**) both in 25% yield. The structural assignment for **5a** was based upon its conversion to, and com-



5a, R = CH_3
b, R = OH
c, R = NH_2

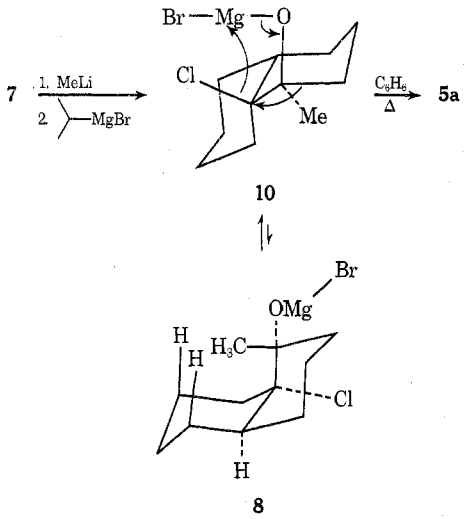
parison with an authentic sample of, the cis amide **5c**. Since pure *trans*-9-chloro-1-decalone (**1**) gave only the *cis*-9-methyl-1-decalone (**4**), it can be safely assumed that the reaction of *cis*-9-chloro-1-decalone was solely responsible for the production of **5a**. For *cis*-9-chloro-1-decalone two conformations **6** and **7** are possible.[8,9]



An examination of molecular models clearly revealed that the axial approach of methyllithium to the carbonyl carbon in **6** (side opposite the chloro group) is blocked by the two axial hydrogens shown. Thus, if formed, the cis chlorohydrin molecule (–OH and –Cl cis) will exist overwhelmingly in conformation **10**, not **8**. The latter **8** is a necessary precursor for the formation of *trans*-9-methyl-1-decalone (**9**). The conspicu-

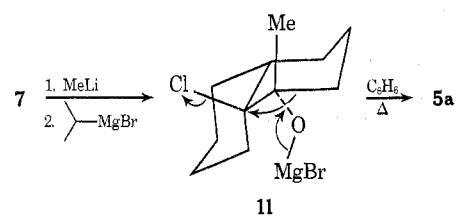
(3) M. Tiffeneau and B. Tchoubar, *C. R. Acad. Sci.*, **198**, 941 (1934); T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.*, **73**, 1993 (1951); A. S. Hussey and R. R. Herr, *J. Org. Chem.*, **24**, 843 (1959).
(4) A. J. Sisti, *ibid.*, **35**, 2670 (1970), and references cited therein.
(5) A. J. Sisti and A. C. Vitale, *Tetrahedron Lett.*, 2269 (1969).
(6) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965).
(7) P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Wiley, New York, N. Y., 1962, p 400.
(8) H. E. Zimmerman and A. Mais, *J. Amer. Chem. Soc.*, **81**, 3644 (1959).
(9) E. J. Corey, *ibid.*, **75**, 2301 (1953).

ous lack of production of **9** offered the experimental verification for the conformational preference of **10** over conformer **8**. The alternative approach of methyllithium to the carbonyl carbon in **6** is precluded as a result of the hindrance furnished by the chloro group. With regard to the conformer **7**, inspection of molecular models revealed that the approach of methyllithium to the carbonyl carbon from the equatorial side will result in the production of the halohydrin **10**, which when converted to its magnesium salt and decomposed would yield **5a** (eq 3). Alternatively, the preferred



(3)

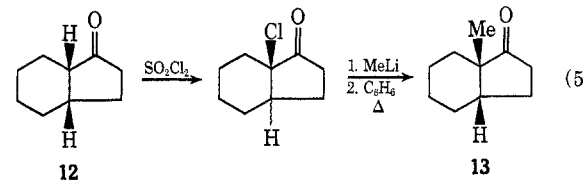
axial approach of methyllithium (conformer **7**) would yield the halohydrin **11**, whose geometry (–OH and –Cl trans) is apparently unfavorable to rearrangement. However, Geissman and Akawie[3] have demonstrated that in the cyclohexyl system a trans diequatorial alignment does not prevent the pinacol-type rearrangement, undoubtedly due to the proximity of the involved equatorial groups. Thus, the magnesium salt of the halohydrin **11** was also expected to yield **5a** as depicted (eq 4).



(4)

Therefore, it may be concluded that the rearrangement of the magnesium salts of the chlorohydrins arising from the addition of methyllithium to *cis*-9-chloro-1-decalone can produce *only* methyl *cis*-hexahydroindan-3*a*-yl ketone (**5a**) and that the lack of production of *trans*-9-methyl-1-decalone (**9**) is reasonably ascribed to the free-energy difference between conformers **8** and **10**.

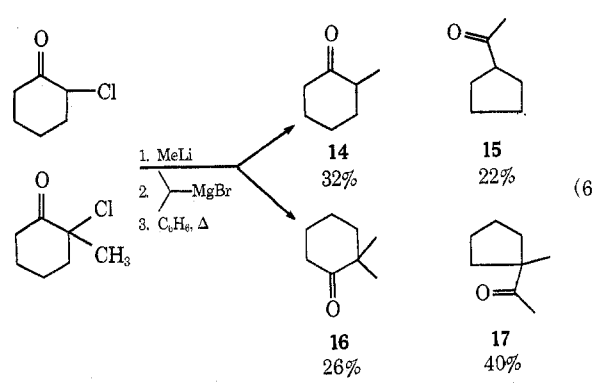
The stereoselective introduction of an angular methyl group was next attempted on the *cis*-perhydro-1-indanone (**12**) system. The ketone **12** reacted with sulfuryl chloride to yield presumably a mixture of *cis*- and *trans*-8-chlorohydrindan-1-one (cis isomer should be preferred[10]). After treatment of the chloro ketone with methyllithium at low temperatures the reaction mixture was refluxed in benzene and produced *cis*-8-methylhydrindan-1-one (**13**) in 5% yield. A large amount of nondistillable polymeric material remained after the removal of **13** (eq 5). The structural assign-



(5)

ment for **13** was based upon infrared and nmr spectra and by its conversion to a known derivative. The angularly methylated product **13** must be produced from the reaction of *trans*-8-chlorohydrindan-1-one. The approach of the methyllithium to the carbonyl carbon in the latter compound will be from the least hindered side, opposite the chloro group, resulting in the production of the lithium salt of the halohydrin with the prescribed geometry necessary for the rearrangement to occur (–OLi and –Cl cis). Thus the rearrangement will result in the production of **13**. A possible rationale for the poor yield obtained of **13** may be due to the deviation from a coplanar arrangement of the migrating methyl and departing chloro groups in the five-membered ring. This deviation should result in a relatively unfavorable energy of activation and thereby cause the poor yield of the rearrangement product. Noteworthy are the results of Mitchovitch,[11] who reported poor yields of 2-methyl- and 2-phenylcyclopentanone when 2-chlorocyclopentanone was treated with methylmagnesium and phenylmagnesium bromides followed by rearrangement of the respective magnesium salts of the resultant halohydrins. The poor results reported may also be attributed to the deviation from a coplanar arrangement of the migrating methyl (or phenyl) and departing chloro groups. No rearrangement products were isolated from the reaction of methyllithium with the cis chloro ketone.

The application of the new synthetic sequence for methylation was concluded with cyclohexanone and 2-methylcyclohexanone, the results of which are presented (eq 6).



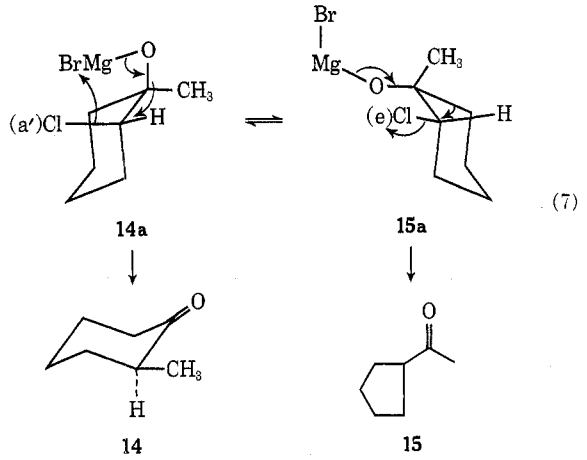
(6)

The approach of the reagent, methyllithium, to the carbonyl carbon in 2-chlorocyclohexanone should be from the side opposite the chloro group; thus one should obtain the cis halohydrin (hydroxyl and chloro groups cis) whose composition should be a mixture of two conformational isomers **14a** and **15a**. The two conformational isomers, when converted to their mag-

(10) D. W. Mathieson, *J. Chem. Soc.*, 3248 (1953).

(11) V. Mitkovitch, *C. R. Acad. Sci.*, **200**, 1601 (1935).

nesium salts and subsequently decomposed, should produce, respectively, **14** and **15** (eq 7). The pref-



(7)

14a **15a**

14 **15**

erential production of **14** over **15** may be attributed to the higher relative energy level for the transition state for the formation of **15** compared to **14**. The latter may be associated with a *six-membered ring* going to a *five-membered ring*. It should be noted that the trans halohydrin (approach of methyllithium from the same side as the chloro group) can only give **15**. Vavon[12] and Tiffeneau[13] previously reported results slightly different from our own; namely, the former reported 2 parts of **14** and 1 part of **15** and the latter "mostly" **14** and a "small amount" of **15**. The discrepancies are undoubtedly attributed to the different analytical methods employed (vpc by us and separation by semicarbazones by them).[14]

When the sequence was conducted with 2-chloro-2-methylcyclohexanone (eq 6) the results favored, in this instance, the ring contraction product **17** over the product resulting from methyl migration **16**. A rationale here without definitive stereochemical information would be doubtful and therefore will be omitted at this point.

Experimental Section

General.—Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected, as are the boiling points. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Ir, uv, and nmr spectra were determined with a Perkin-Elmer Model 257 spectrophotometer, a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer, and a Varian A-60 nuclear magnetic resonance instrument, respectively. Analytical vpc analyses were performed with an F & M Scientific Model 720 dual column programmed temperature instrument and preparative vpc separations were performed with an F & M Scientific Model 776 Prepmaster Jr. A Nester/Faust Manufacturing Corp. annular teflon spinning band distillation column was used for all spinning band distillations.

9-Chloro-*trans*-1-decalone (1) was prepared according to the procedure of House,[6] mp 39–40° (lit.[6] mp 40–41°).

***cis*-9-Chloro-1-methyl-*trans*-1-decalol** (2).—Under a nitrogen atmosphere 19.0 ml of 2.05 *M* methyllithium (Alfa Inorganics, Inc.) in ether (0.031 mol + 25% excess) was added dropwise to a stirred solution of 5.8 g (0.031 mol) of **1** in 75 ml of anhydrous ether at Dry Ice–acetone temperature. The resulting mixture was stirred for 1.5 hr at Dry Ice–acetone temperature and then for 2 hr at −5°. Hydrolysis was achieved with a saturated solution of ammonium chloride and the resulting halohydrin **2** was taken up in ether, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to a clear yellow oil: nmr (CCl_4) τ 8.72 (s, 3 H, $-CH_3$); ir (film) 3350 and 3460 cm^{-1} (–OH); an instantaneous precipitate with alcoholic silver nitrate.

***cis*-9-Methyl-1-decalone** (**4**).—A solution of 6.1 g (0.030 mol) of the crude halohydrin **2** in 100 ml of anhydrous benzene was stirred under a nitrogen atmosphere and immersed in an ice bath until the benzene solution was partially crystallized. To this partially crystallized solution 23.2 ml (0.030 mol) of 1.30 *N* isopropylmagnesium bromide[15] was added dropwise so that the temperature of the reaction vessel did not exceed room temperature. After the addition the reaction mixture was refluxed for 2 hr, then hydrolyzed with a saturated ammonium chloride solution, and the organic layer was separated, dried ($MgSO_4$), and filtered. After the removal of solvent under reduced pressure, the residue was distilled on the spinning band column. The distillate contained 2.9 g (0.018 mol) (58%) of **4**: bp 50–52° (0.3 mm) [lit.[16] bp 100° (7–8 mm)]; identification by vpc (TCEP 4-ft column, 175°) and ir, each of which gave a perfect comparison with an authentic sample;[17] nmr (CCl_4) τ 8.85 (s, 3 H, $-CH_3$); 2,4-dinitrophenylhydrazone mp 163–164° (lit.[16] mp 164–165°), and the oxime mp 109–110° (lit.[16] mp 109–110°).

In another run 23.7 ml (0.052 mol) of 2.30 *M* methyllithium was added dropwise to a stirred solution of 9.72 g (0.052 mol) of **1** in 125 ml of anhydrous ether, at Dry Ice–acetone temperature under a nitrogen atmosphere. The mixture was stirred for 1.5 hr at Dry Ice–acetone temperature and then for 2 hr at −5°. The temperature of the reaction mixture was brought slowly to room temperature and the ether was removed by distillation simultaneously with the addition of anhydrous benzene and finally refluxed for 3 hr. The reaction mixture was worked up as above and after distillation on the spinning band column there was obtained 5.4 g (0.032 mol) (62%) of **4**, bp 50–52° (0.3 mm) [lit.[16] bp 100° (7–8 mm)].

Methyl *cis*-Hexahydroindan-3*a*-yl Ketone (**5a**).—Into a flask was placed 18.7 g (0.10 mol) of an approximately equal mixture of *cis*- and *trans*-9-chloro-1-decalone[6] in 100 ml of anhydrous ether to which was added 54.4 ml of 2.30 *M* methyllithium (0.100 mol + 25% excess) in ether as described above for the preparation of **2**. The resulting 20 g of crude halohydrin was dissolved in 300 ml of anhydrous benzene and was treated with 80 ml of 1.25 *M* isopropylmagnesium bromide[15] as previously described above for the preparation of **4**. The residue was distilled on a spinning band column and afforded a first fraction containing 4.2 g (0.025 mol) (25%) of **5a** as a colorless liquid, bp 38° (0.04 mm), followed by a second fraction of 4.0 g (0.024 mol) (24%) of **4**, bp 42° (0.03 mm) [lit.[16] bp 100° (7–8 mm)].

Compound **5a** gave ir (film) 1690 cm^{-1} (C=O); nmr (CCl_4) τ 7.90 (s, 3 H, $COCH_3$); 2,4-dinitrophenylhydrazone (EtOH) mp 134–135°.

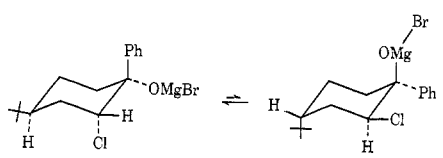
Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.95; H, 6.40; N, 16.17. Found: C, 59.13; H, 6.49; N, 16.26.

A haloform reaction[18] converted **5a** to *cis*-hexahydroindan-8-carboxylic acid, mp 42–43° (lit.[19] mp 43.5–44.5°); the acid was

(12) G. Vavon and A. Perlin-Borrel, *Bull. Soc. Chim. Fr.*, **51**, 994 (1932).

(13) M. Tiffeneau and B. Tchoubar, *C. R. Acad. Sci.*, **199**, 360 (1934).

(14) It is noteworthy to mention that recent work [F. G. Bordwell and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5933 (1970)] tends to substantiate the rationale presented in eq 7. The reaction product of *trans*-4-*tert*-butyl-2-chlorocyclohexanone with phenylmagnesium bromide produced the magnesium salt of 4*e*-*tert*-butyl-2*a*-chloro-1*a*-phenylcyclohexan-1*e*-ol, which upon decomposition in refluxing xylene produced *no ring contraction product* but mostly *cis*-4*e*-*tert*-butyl-2*e*-phenylcyclohexanone. The presence of the *tert*-butyl group provides the free energy difference between the two conformers, so that the molecule exists overwhelmingly with the *tert*-butyl



group in the equatorial position. Thus the production of the ring contraction product was essentially precluded.

(15) The isopropylmagnesium bromide was prepared and titrated according to the procedure of Gilman [H. Gilman and E. Zolliner, *J. Amer. Chem. Soc.*, **51**, 1576 (1929)].

(16) W. S. Johnson, *ibid.*, **65**, 1317 (1943).

(17) Dr. W. S. Johnson graciously supplied the authentic sample containing 85% *cis*- and 15% *trans*-9-methyl-1-decalone.

(18) L. T. Sandborn and E. W. Bousquet, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 526.

(19) W. G. Dauben, J. W. McFarland, and J. B. Rogan, *J. Org. Chem.*, **26**, 297 (1961).

converted to the amide **5c** *via* the acid chloride. The *cis*-hexahydroindan-8-carboxylamide (**5c**), mp 109–110° (lit.[19] mp 109–110°), showed no depression in melting point when admixed with an authentic sample.[20]

***cis*-Perhydro-1-indanone (12).**—The compound was prepared by the procedure described by Johnson[21] and Mathieson:[10] bp 64–65° (3.5 mm) [lit.[10] bp 72–73° (6 mm)]; ir (film) 1731 cm^{-1} (C=O); nmr (CCl_4) τ 7.7–8.0 (m, $CHCOCH_2$).

8-Chlorohydrindan-1-one.—A solution of 29 g (0.209 mol) of **12** in 160 ml of carbon tetrachloride was maintained at 19–24° while a solution of 19.7 ml (0.245 mol) of sulfuryl chloride in 85 ml of carbon tetrachloride was added dropwise with stirring over a 2-hr period. The resulting solution was stirred for 3 hr at 24° and then washed successively with water, aqueous sodium bicarbonate, and aqueous sodium chloride. The organic solution was then dried ($MgSO_4$) and the solvent was removed under vacuum. Distillation with a 10-in. Vigreux column gave a fraction of 28.4 g (0.165 mol) (79%) of 8-chlorohydrindan-1-one (presumably a cis–trans mixture): bp 62° (0.8 mm); ir (film) 1753 (C=O), 757 cm^{-1} (CCl); nmr (CCl_4) τ 7.5–7.8 (m, $COCH_2$); positive and instantaneous alcoholic silver nitrate test.

Anal. Calcd for $C_9H_{13}ClO$: C, 62.60; H, 7.54. Found: C, 62.40; H, 7.60.

***cis*-8-Methylhydrindan-1-one (13).**—Under a nitrogen atmosphere 36.2 ml (0.0870 mol) of 2.40 *M* methyllithium in ether was added dropwise to a stirred solution of 15 g (0.0870 mol) of 8-chlorohydrindan-1-one in 200 ml of anhydrous ether at Dry Ice–acetone temperature. The resulting mixture was stirred for 1.5 hr at the latter temperature and then for 2 hr at −5°. The reaction mixture was allowed to come to room temperature and was stirred for 2 hr. The ether was removed by distillation while anhydrous benzene was simultaneously added. After the benzene reaction mixture was refluxed for 3 hr, the reaction product was worked up as described above, yielding a clear yellow, very viscous oil. Distillation with a 10-in. Vigreux column produced 0.55 g (0.0040 mol) (5%) of **13**: bp 42° (0.8 mm) [lit.[22] bp 106 (20 mm)]; ir (film) 1726 cm^{-1} (C=O); nmr (CCl_4) τ 9.0 (s, 3 H, $-CH_3$); 2,4-dinitrophenylhydrazone mp 140–141° (lit.[22] mp 140.5–141°). The residue, 12 g, was a nondistillable solid polymeric material.

2-Chloro-2-methylcyclohexanone was prepared according to the procedure described by Warnhoff,[23] bp 90–92° (25 mm) [lit.[23] bp 94–96° (27 mm)].

***cis*-2-Chloro-1,2-dimethylcyclohexanol** was prepared using 15 g (0.10 mol) of 2-chloro-2-methylcyclohexanone in 100 ml of anhydrous ether and 59.6 ml of 2.05 *M* methyllithium according to the procedure for the preparation of the halohydrin **2**. After the work-up, 16 g of crude halohydrin was recovered: ir (film) 3560 and 3470 cm^{-1} (–OH); an instantaneous white precipitate with alcoholic silver nitrate.

2,2-Dimethylcyclohexanone (16) and 1-Acetyl-1-methylcyclopentane (17).—To a solution of 16 g of the previously prepared crude halohydrin in 300 ml of anhydrous benzene was added, dropwise, 80 ml (0.10 mol) of 1.25 *M* isopropylmagnesium bromide[15] according to the procedure described above for the preparation of **4**. After decomposition the product was distilled on a 10-in. Vigreux column, yielding 13 g (0.066 mol) (66%) of a colorless oil, bp 68–69° (33 mm), consisting of a mixture of two parts of **16** to three parts of **17** as analyzed by vpc (20% TCEP on Chromosorb P, 4 ft × 0.25 in. column, 100°). The isomeric ketones **16** and **17** were satisfactorily separated by preparative vpc (20% Carbowax on 60–80 mesh Chromosorb W acid-washed, 80 × 0.75 in. column, 80°).

Compound **17** was identified by vpc (TCEP, 4 ft × 0.25 in. column, 100°) and ir, each of which gave a perfect comparison with an authentic sample.[24] The semicarbazone of **17** was also prepared, mp 140–141° (lit.[25] mp 140–141°).

Compound **16** was identified by its 2,4-dinitrophenylhydrazone, mp 140–141° (lit.[26] mp 140–142°), and its semicarbazone mp, 198–199° (lit.[27] mp 199–200°).

***cis*-2-Chloro-1-methylcyclohexanol** was prepared using 13.3 g (0.100 mol) of 2-chlorocyclohexanone (Aldrich Chemical Co.) in 200 ml of anhydrous ether and 55 ml of 2.3 *M* methyllithium in ether according to the above procedure for the preparation of the halohydrin **2**. After work-up 14.4 g of crude halohydrin was recovered, ir (film) 3560 and 3480 cm^{-1} (–OH) and an instantaneous precipitate with alcoholic silver nitrate.

2-Methylcyclohexanone (14) and Acetylcyclopentane (15).—To a solution of 14.4 g of the prevously prepared crude halohydrin in 300 ml of anhydrous benzene, 80 ml of 1.25 *M* isopropylmagnesium bromide[15] was added dropwise according to the above described procedure for the preparation of **4**. The residue was distilled on a 10-in. Vigreux column to give 6.1 g (0.054 mol) (54%) of a colorless liquid, bp 45–50° (8 mm). It consisted of three parts of **14** to two parts of **15** as analyzed by vpc (20% TCEP on Chromosorb P, 4 ft × 0.25 in. column, 100°). The isomeric ketones **14** nd **15** were successfully separated by preparative vpc (20% Carbowax on 60–80 mesh Chromosorb W acid washed, 80 × 0.75 in. column, 80°).

Compound **14** was identified by vpc (TCEP 4 ft × 0.25 in. column, 100°) and ir, each of which gave a perfect comparison with an authentic sample (Aldrich Chemical Co.).

Compound **15** was identified by ir (film) 1715 cm^{-1} (C=O); nmr (CCl_4) τ 7.97 (s, 3 H, $COCH_3$); semicarbazone mp 143–144° (lit.[27] mp 145°) and 2,4-dinitrophenylhydrazone mp 124–125° (lit.[28] mp 127°).

Registry No.—**2**, 23472-37-9; **4**, 770-62-7; **5a**, 36444-55-0; **5a** 2,4-DNP, 36744-51-1; **12**, 2826-65-5; **13**, 13025-91-7; **14**, 583-60-8; **15**, 6004-60-0; **16**, 1193-47-1; **17**, 13388-93-7; *cis*-8-chlorohydrindan-1-one, 36744-54-4; *trans*-8-chlorohydrindan-1-one, 36744-55-5; *cis*-2-chloro-1,2-dimethylcyclohexanol, 36744-56-6; *cis*-2-chloro-1-methylcyclohexanol, 19324-75-7.

(20) We are grateful to Dr. W. G. Dauben for supplying a sample of **5c**.

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(22) W. S. Johnson, *ibid.*, **66**, 215 (1944).

(23) E. W. Warnhoff, D. G. Martin, and W. S. Warnhoff, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 162.

(24) An expression of thanks to Dr. H. Hart for supplying a sample of **17**.

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