reacted 2-chloro-1,1,1-triphenylethane, and nonvolatile neutral products. During the course of work-up of the reaction products a crystalline material, mp 151.0–152.5° (from acetone), was isolated.

Anal. Calcd for 1:1 compound of $C_{20}H_{17}Cl$ and $C_{21}H_{18}O_2$: C, 82.74; H, 5.93; Cl, 5.96, average mol wt, 297.5 Found: C, 82.59; H, 6.14; Cl, 5.32; mol wt (acetone), 289.

The above analysis is in essential agreement with a 1:1 compound of 2-chloro-1,1,1-triphenylethane[61] (mp 101.0–101.8°) and 2,2,3-triphenylpropanoic acid[61] (mp 132.0–133.0°). This postulated composition was qualitatively confirmed[62] by glpc, nmr, uv, and mass spectral analyses.

Registry No.—**8c**, 33884-94-5; **9a**, 33884-95-6; **11**, 33884-96-7; 4-chloro-1,1,1-triphenylbutane, 33884-97-8; 5-chloro-1,1,1-triphenylpentane, 33884-98-9; 1,1,1-triphenylethane, 5271-39-6; lithium, 7439-93-2; potassium, 7440-09-7; cesium, 7440-46-2; sodium, 7440-23-5; 1,1,1-triphenylpentane, 13630-39-2; 2-chloro-1,1,1-triphenylethane, 33885-01-7; 5,5,5-triphenylpentanenitrile, 33885-02-8; 5,5,5-triphenylpentanoic acid, 33885-03-9; methyl 5,5,5-triphenylpentanoate, 33885-04-0; 2,2,5-triphenylpentanoic acid, 33885-05-1; 1,1,4-triphenylbutane, 33885-06-2; 6,6,6-triphenylhexanenitrile, 33885-07-3; 6,6,6-triphenylhexanoic acid, 33885-08-4; 1,1,5-triphenylpentanol-1, 33885-09-5; 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene-2,7-d_2, 33885-10-8; 1:1 compound of 2-chloro-1,1,1-triphenylethane and 2,2,3-triphenylpropanoic acid, 33885-11-9.

(62) We are indebted to Mr. Thomas H. Longfield for this identification.

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The Influence of Chelation on the Grignard Reactions of Some β-Hydroxy Ketones[1]

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β-Hydroxy ketones, having one of the oxygen-containing functions situated on a five- or six-membered carbon ring and the other on a side chain, undergo highly stereoselective Grignard reactions except when chelation is sterically inhibited. Thus, 2-α-hydroxyalkyl- (or 2-hydroxyaryl-) cyclopentanones and cyclohexanones yield pure diols. *cis*-2-Acylcyclopentanols also undergo stereospecific additions whereas similar reactions of *trans*-acylcyclopentanols resulted in poor yields and low stereoselectivity. By contrast, *trans*-2-acylcyclohexanols reacted stereospecifically and in high yields with Grignard reagents. The results are correlated with the readiness of reactants to form chelates.

The preferential formation of a major diastereomer in Grignard reactions of open-chain α-hydroxy ketones, in which the carbonyl group is adjacent to a chiral center, has been explained by the intermediacy of a chelate.[2] Similar reactions of β-hydroxy ketones were found to be less stereoselective and the results were explained by an "open-chain" instead of a "cyclic" transition state.[3]

Grignard reactions of β-hydroxy ketones in which one of the oxygen-containing functions is situated on a five- or six-membered carbon ring constitute the present study. The purpose of this investigation was to correlate the results of reactions (expressed in stereoselectivity and yields) with the stereochemical readiness of the organic substrates to form chelates with the metallic ion.

Results

Stereoisomeric *cis*- and *trans*-2-hydroxycyclopentanecarboxylic ethyl esters were used for the synthesis of several β-hydroxy ketones in the cyclopentane series. The chromatographic separation into cis (**1a**) and trans (**1b**) esters was achieved and therefore the previously used[4] procedure *via* separation of their 3,5-dinitrobenzoates was unnecessary. The difference between the chemical shifts of the methylene quartet of the ester function in the nmr spectrum proved to be a better criterion for the determination of isomeric purity than the previous assignment based on the band width of the proton adjacent to the hydroxyl group.[4b] Ketols **2** and **3** (Table I) were prepared from *cis*-hydroxy ester **1a** by the corresponding Grignard reactions followed by Jones oxidation. Six-membered homologs **7** and **8** were preferentially prepared from *trans*-2-hydroxycyclohexanecarboxylic esters by the same sequence. 2-Benzhydrylcyclopentanone **6** was obtained by dehydration of hydroxy ketone **2** to 2-benzylidenecyclopentanone and subsequent hydrogenation. *cis*- and *trans*-2-benzoyl- and -2-acetylcyclopentanols (**20a**, **20b**, **21a**, and **21b**, Table II) were prepared from *cis*-2-hydroxycyclopentanenitrile and MeMgBr or PhMgBr, respectively, followed by the hydrolysis of formed imines. Equilibration occurred during these reactions and the mixture of cis and trans ketols was separated by chromatography. Compounds **20a** and **20b** were also obtained from the reaction of *trans*-hydroxy ester **1b** with PhMgBr (see Experimental Section). Stereochemical assignments in this series were based on the differences in hydroxyl stretching frequencies in the infrared spectra: unlike *cis*-2-acylcyclopentanols, the trans isomers do not show the presence of intramolecular hydrogen bonding (Table III). Independent synthesis of diols **24a** and **27a** from *cis*-hydroxy ester **1a** served as an additional proof for the cis configuration of compounds **20a** and **21a**.

(1) A portion of this work has appeared in preliminary form: E. Ghera and S. Shoua, *Chem. Commun.*, 398 (1971).

(2) (a) D. J. Cram and K. R. Kopecky, *J. Amer. Chem. Soc.*, **81**, 2748 (1959); (b) D. J. Cram and D. R. Wilson, *ibid.*, **85**, 1245 (1963).

(3) T. J. Leitereg and D. J. Cram, *ibid.*, **90**, 4019 (1968).

(4) (a) J. Pascual and J. Castells, *ibid.*, **74**, 2899 (1952); (b) H. Baumann, N. C. Franklin, and H. Mohrle, *Tetrahedron*, **23**, 433 (1967).

TABLE I

GRIGNARD REACTIONS OF 2-SUBSTITUTED CYCLOALKANONES

Reactant	Reagent	Product[a]	Overall yield, %	Stereoselectivity, %
		$n = 1$		
2, $R_1 = R_2 = Ph$; $R_3 = OH$	MeMgBr	**11**, $R_4 = OH$; $R_5 = Me$	68	100
3, $R_1 = R_2 = Me$; $R_3 = OH$	PhMgBr	**12**, $R_4 = OH$; $R_5 = Ph$	60	100
4,[b] $R_1 = Ph$; $R_2 = H$; $R_3 = OH$	MeMgJ	**13**, $R_4 = OH$; $R_5 = Me$	71	100
5,[c] $R_1 = R_2 = H$; $R_3 = OH$	PhMgBr	**14**, $R_4 = OH$; $R_5 = Ph$	32[d]	100
6, $R_1 = R_2 = Ph$; $R_3 = H$	MeMgJ	**15a**, $R_4 = OH$; $R_5 = Me$	78[e]	56[e]
	MeMgBr	**15b**, $R_4 = Me$; $R_5 = OH$	81[f]	75[f]
		$n = 2$		
7, $R_1 = R_2 = Ph$; $R_3 = OH$	MeMgBr	**16**, $R_4 = OH$; $R_5 = Me$	38[g]	100
8,[h] $R_1 = R_2 = Me$; $R_3 = OH$	PhMgBr	**17**, $R_4 = OH$; $R_5 = Ph$	27[i]	100
9,[j] $R_1 = Ph$; $R_2 = H$; $R_3 = OH$	MeMgBr	**18**, $R_4 = OH$; $R_5 = Me$	78	100
10,[k] $R_1 = Me$; $R_2 = H$; $R_3 = OH$	PhMgBr	**19a**, **19b** $R_4 = OH$; $R_5 = Ph$	54	100

[a] Data on reaction conditions and newly prepared compounds are given in the Experimental Section and Table IV; the limit of detection for the minor diastereomer is <1%. [b] Pure diastereomer. [c] *Cf.* T. Takahashi, A. Kato, and S. Matsuoka, *Chem. Abstr.*, **54**, 4543*f* (1960). [d] α-Methylbenzyl alcohol and cleavage products were also formed. [e] For MeMgJ. [f] For MeMgBr; the values represent per cent of **15a** in the epimeric mixture. [g] Starting material and diphenylmethylcarbinol were also isolated. [h] J. Wolinsky, M. Senyek, and S. Cohen, *J. Org. Chem.*, **30**, 3207 (1965). [i] About 50% of starting material was recovered in variable reaction conditions. [j] *Cf.* ref 7. [k] *Cf.* F. Fries and F. Broich, *Chem. Abstr.*, **53**, P7056*g* (1959). Compound **10** consisted of a diastereomeric mixture inseparable by distillation or chromatography, as evidenced by nmr spectroscopy; both products, **19a** and **19b**, were cis diols (see Experimental Section).

TABLE II

GRIGNARD REACTIONS OF 2-ACYLCYCLOALKANOLS

Reactant	Reagent	Product[a]	Overall yield, %	Stereoselectivity, %[b]
		$n = 1$		
20a, R = Ph; $R_1 = OH$; $R_2 = H$	PhMgBr	**24a**, $R_3 = Ph$	72	
	MeMgBr	**25a**, R = Ph; $R_3 = Me$	76	93
		26a, R = Me; $R_3 = Ph$	6	
20b, R = Ph; $R_1 = H$; $R_2 = OH$	PhMgBr	**24b**, $R_3 = Ph$	7[c]	
	MeMgBr[d]	**25b**, $R_3 = Me$; R = Ph	16	60
		26b, R = Me; $R_3 = Ph$	11	
21a, R = Me; $R_1 = OH$; $R_2 = H$	PhMgBr	**26a**, R = Me; $R_3 = Ph$	73	100
	MeMgBr	**27a**, $R_3 = Me$	70	
21b, R = Me; $R_1 = H$; $R_2 = OH$	MeMgBr	**27b**, $R_3 = Me$	15	
		$n = 2$		
22a, R = Ph; $R_1 = OH$; $R_2 = H$	PhMgBr	**28a**,[e] $R_3 = Ph$	41	
	MeMgBr	**29a**, R = Ph; $R_3 = Me$	49	100
22b, R = Ph; $R_1 = H$; $R_2 = OH$	PhMgBr	**28b**,[e] $R_3 = Ph$	82	
	MeMgBr	**29b**, R = Ph; $R_3 = Me$	82	100
23, R = Me; $R_1 = H$; $R_2 = OH$	PhMgBr	**30b**, R = Me; $R_3 = Ph$	83	100
	MeMgBr	**31b**,[e] $R_3 = Me$	84	

[a] The substituents not mentioned in the product are the same as in the reactant. [b] Values are given for reactions in which a new chiral center is formed and represent per cent of the major isomer in the diastereomeric mixture. [c] All other products from this reaction were obtained in about the same yields and by the manner shown for the reaction of **1b** and PhMgBr (see Experimental Section). [d] The reaction mixture yielded, in order of chromatographic elution, 1-benzoylcyclopentene, **20b**, **26b**, and **25b**. [e] *Cf.* ref 21.

All Grignard reactions of hydroxy ketones were carried out with excess of reagent and the crude reaction mixtures were submitted to tlc and nmr analysis. Isomeric diols (if present) usually showed chemical-shift differences for the methyl proton signals and for the protons adjacent to the hydroxyl groups. All diols were separated from by-products by column chromatography.

Hydroxy ketones **2**–**5** (Table I) afforded pure diols to which the cis configuration was assigned on the basis of presence of intramolecular hydrogen bonding in the infrared spectra. Trans diols (*e.g.*, **25b** or **26b**, Table III) were devoid of intramolecularly bonded OH.[5]

In the cyclohexane series, similar reactions of hydroxy ketones **7**–**10** also resulted in the formation of cis diols exclusively. The assignment of configuration was based on the known preference for trans attack in 2-

(5) The relative large torsional angles for vicinal trans substituents in cyclopentanes are responsible for this difference; see E. L. Eliel, N. A. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 203.

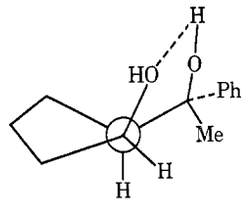
TABLE III
INFRARED HYDROXYL STRETCHING FREQUENCIES[a]

Compound	ν_{free}[b]	ν_{bonded}
3	3623 (sh)	3529 (s)
8	3633 (sh)	3548 (s)
12	3637 (w)	3509 (s)
20a	3646 (sh)	3509 (s)
20b	3629	
21a		3537 (br)
21b	3630	
25a	3673 (w)	3506
26a	3634 (w)	3526
25b	3630	
26b	3611	
27a	3635 (w)	3507 (s)

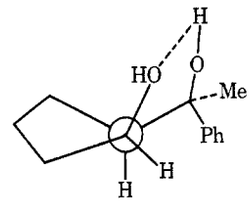
[a] Recorded on a Beckman IR-7 spectrophotometer. The concentration was 0.02 *M* in Spectrograde CCl_4. [b] s, strong; sh, shoulder; w, weak; br, broad.

substituted cyclohexanones[6] and previous observations.[7] In variance with compounds **2** and **3**, their six-membered homologs **7** and **8** reacted in lower yields and significant amounts of starting material were recovered. The reactions of 2-benzhydrylcyclopentanone (**6**, devoid of a chelating hydroxyl group) with MeMgI and MeMgBr were less stereoselective and the configurational assignments of the obtained isomeric alcohols **15a** and **15b** were based on nmr evidence (the methine proton was deshielded when cis oriented to the hydroxyl group).

Grignard reactions of *cis*-acylopentanols (Table II) were characterized by good yields and high stereoselectivity. Thus, *cis*-2-benzoylcyclopentanol (**20a**) afforded, with MeMgBr, the diol **25a** (93% stereoselectivity), whereas *cis*-2-acetylcyclopentanol and PhMgBr yielded its diastereomer (**26a**) exclusively. The nmr spectra were in agreement with the shown configurations in which the stablest conformation implies intramolecular hydrogen bonding and pseudoequatorial orientation for the side chain.



25a

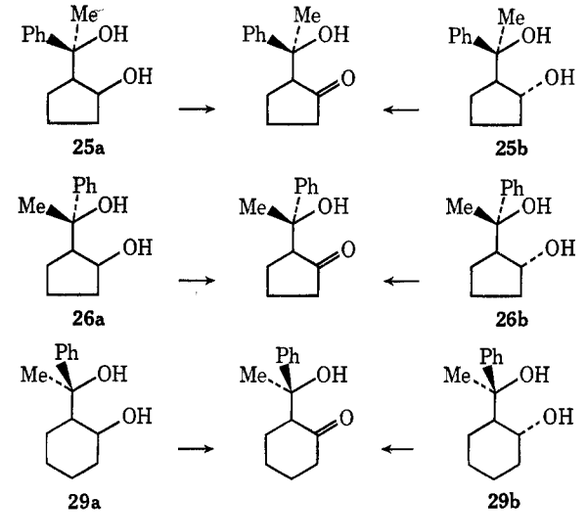


26a

In **26a** the proton adjacent to the hydroxyl group is shielded (δ 3.77) owing to the anisotropy of the phenyl group (above or below the plane of the aromatic ring), whereas in **25a** it is not (δ 4.64). Conversely, the methyl group is relatively nearer to the secondary hydroxyl group in **25a** (δ 1.70) than in **26a** (δ 1.38).

The corresponding *trans*-2-acylcyclopentanols behaved very differently in terms of yields of diols and stereoselectivity of reactions. Unlike the cis isomer, *trans*-2-benzoylcyclopentanol (**20b**) afforded with MeMgBr only small amounts of diastereomeric diols **25b** and **26b** and some of the starting material was recovered. The stereochemical assignments for trans diols **25b** and **26b** were based on oxidation results and correlation with cis diols (Scheme I).

SCHEME I



The particular reaction of **20b** and PhMgBr afforded (in order of chromatographic elution) 1-benzoylcyclopentene (24%), cis ketol **20a** (13%), trans diol **24b** (8%), and trans ketol **20b** (28%). α-Methylbenzyl alcohol was also obtained (in amounts varying between 5 and 20% of the total material) even when the reaction was conducted under pure nitrogen.[8] The latter compound was not detected in an identical reaction of **20a** and its formation might be due to lower reactivity of **20b** toward PhMgBr.[9]

In reactions paralleling those of 2-acylcyclopentanols, *cis*-hydroxy ester **1a** afforded readily the corresponding diols whereas trans isomer **1b** gave results similar to those obtained from trans ketols **20b** and **21b**. Hence the conversion, *trans*-hydroxy ester → trans ketol takes place normally.

In contrast to *trans*-2-acylcyclopentanols, Grignard reactions of *trans*-2-acylcyclohexanols proceeded with complete stereospecificity and very good yields; the pure diol (**29b**) obtained from **22b** and MeMgBr was diastereomeric with diol **30b**, formed exclusively in the reaction of **23b** and PhMgBr. The configurational assignment for **29b** was based on the chemical shift of the proton adjacent to the hydroxyl group which showed strong shielding (δ 3.11) owing to the anisotropy of the phenyl group in a hydrogen-bonded conformation. In the cis series, 2-benzoylcyclohexanol **22a** afforded comparatively lower yields of diols. Jones oxidation of the diol **29a** and correlation with the diol **29b** (Scheme I) provided the configurational assignment.

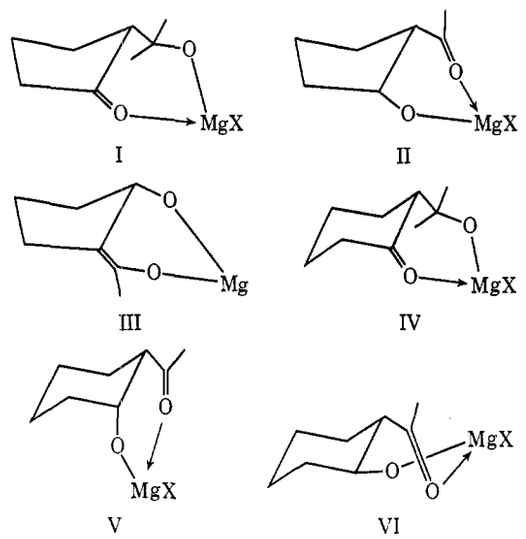
In agreement with the above results, Grignard reactions of *trans*-2-hydroxycyclohexanecarboxylic esters also afforded significantly higher yields of diols than the corresponding *cis*-hydroxy esters (see Experimental Section).

(6) G. Di Maio, M. T. Pellegrini, and P. A. Tardella, *Ric. Sci.*, 240 (1968); *Chem. Abstr.*, **69**, 77064f (1968).

(7) H. E. Zimmermann and J. English, *J. Amer. Chem. Soc.*, **76**, 2285 (1954).

(8) The formation of this compound was reported to occur when ether solutions of PhMgBr were exposed to oxygen [*e.g.*, C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955)].

(9) Free radicals were detected in THF solutions of phenyl ketones in presence of PhMgBr and their concentration depended on the concentration of reagents. *Cf.* K. Maruyama, *Bull. Chem. Soc. Jap.*, **37**, 897 (1964).



Discussion

The accepted "reactant-like" transition state for Grignard additions[10] and the stereochemical assignments for the products obtained permit the discussion of results in terms of cyclic models I–VI. In these models a distorted half-chair conformation can probably be assumed for the chelated rings on the basis of tetrahedral orientation of Mg bonds, greater O–Mg bond distances (2.10 Å) and recent conformational studies on 1,3 heterocycles.[11] Inspection of steric models shows that there is a relationship between the conformational and configurational properties of reactants and the stereoselectivity and yields of additions: an orientation of C–O bonds which allows formation of chelates with lesser strain and lesser nonbonded interactions ensures higher yields and stereospecificity in Grignard reactions. Thus, the addition to models I and IV is stereospecific because the "endo" approach (from below) of the reagent is hindered. By contrast, in nonchelated 2-substituted cyclopentanones[12] and cyclohexanones[6] the minor stereoisomeric Grignard adduct was usually also formed. Even the presence of a bulky substituent (in compound **6**) did not prevent the formation of the minor isomer. Recovery of starting material from reactions of compounds **7** and **8** suggests that nonbonded interactions between bulky substituents and ring bonds are stronger in chelates formed from cyclohexane than cyclopentane derivatives[13] and therefore tautomeric shifts enable the formation of less hindered chelates by enol participation.

The Grignard reactions of stereoisomeric 2-acylcyclopentanols permitted to establish the difference in behavior between the isomers able to form chelates and those unable to do so. Model II allowed a stereoselective approach of the reagent (from above) and the addition yields were probably enhanced by bond polarization. By contrast, addition of reagents to *trans*-2-acylcyclopentanols was inhibited and not stereoselective. Isolation of both **20a** and **20b** from the reaction of *trans*-2-benzoylcyclopentanol (**20b**) with PhMgBr and the loss of deuterium in the above compounds (when deuterated **20b** in the α position to the carbonyl was used in this reaction) show that the ketone–enol equilibrium was shifted toward the enol and the chelate (model III) was formed by the flattening of the molecule. 1-Benzoylcyclopentene, which was also obtained in the above reaction, was not formed under similar conditions from the cis isomer **20a** where a trans elimination would favor its formation. Hence the elimination occurred from complex III.

Participation of two (trans) equatorial bonds in the formation of a nonstrained chelate VI ensured stereospecific high-yield addition to *trans*-acylcyclohexanols by the approach of the reagent from the less hindered side (from above). In *cis*-acylcyclohexanols chelate formation involves an axial and an equatorial bond (model V) and the lesser stability of a pseudo cis-fused bicyclic model is reflected mainly in lower yields of diols.

In conclusion, the results obtained indicate the possibility of asymmetric synthesis starting from a variety of acylcycloalkanols.[14]

In open-chain β-hydroxy ketones the cyclic models did not predict the correct addition results and it has been assumed that this may be due to the possible lower stability of six- than five-membered chelated rings.[3] Present results show however that six-membered chelates of β-hydroxy ketones can be readily formed. Hydride reductions of some open-chain β-hydroxy ketones, monosubstituted at the central carbon atom, were reported[15,16] to be stereoselective owing to attack from the less hindered side of a cyclic model, in respect to the α substituent. It seems therefore reasonable to assume that a cyclic model also predominates in the transition state of the reported[3] Grignard reactions of 4-hydroxy-4-phenyl-2-pentanone and 1,3-diphenyl-3-hydroxy-1-butanone, but that the effect bulks of the β substituents, in absence of an α substituent to the carbonyl group, do not exercise an orienting effect.[17] Substitution at the central carbon atom in the presently studied β-hydroxy ketones exercised a decisive orienting effect, when chelation was sterically possible.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ as solvent. Florisil 60–100 mesh was used for column chromatography, if not specified otherwise. Silica gel Merck (0.05–0.2 mm) was used in columns loaded by the "dry column" method[18] (the components were eluted by the standard manner).

Separation of *cis*- and *trans*-2-Hydroxycyclopentanecarboxylic

(10) *Cf.* (a) G. J. Karabatsos, *J. Amer. Chem. Soc.*, **89**, 1367 (1967); (b) M. Cherest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).

(11) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970).

(12) J. P. Battioni, M. L. Capmau, and W. Chodkiewicz, *Bull. Soc. Chim. Fr.*, 976 (1969).

(13) The intramolecular hydrogen bonding is somewhat stronger in compound **3** (i.e., $\Delta\nu$ is greater) than in compound **8** (Table III).

(14) A stereospecific Grignard addition to 1-acyl-2-methoxycyclohexane, part of a thebaine derivative, was reported by K. W. Bentley, D. G. Hardy, and B. Meek, *J. Amer. Chem. Soc.*, **89**, 3273 (1967). In this particular case the approach to one of the carbonyl faces was hindered by the presence of an etheno bridge in the cyclohexane ring.

(15) J. P. Maffrand and P. Maroni, *Bull. Soc. Chim. Fr.*, 1408 (1970).

(16) S. Yamada and K. Koga, *Tetrahedron Lett.*, 1711 (1967).

(17) The assumption of the authors that the stereoselectivity is predicted by an open-chain model was mainly based on results obtained in the reaction of 4-hydroxy-4-phenyl-2-pentanone and PhMgBr. Repeating the determination of the OH stretching frequency in the infrared spectrum of the above hydroxy ketone (in 0.02 *M* CCl_4 solution), we found only a broad absorption between 3480 and 3520 cm^{-1} which is in complete agreement with a chelated (by hydrogen bonding) rotamer.

(18) B. Loev and M. M. Goodman, *Chem. Ind.* (*London*), 2026 (1967).

Ethyl Esters 1a and 1b.—The mixture of stereoisomers[4a] (10 g) was separated by chromatography using the "dry column" method. Elution with pentane and 20% ether afforded first the cis isomer **1a** (6.4 g), nmr δ 4.20 (q, 2, $COOCH_2$–, J = 7 Hz), followed by a few fractions of a mixture of **1a** and **1b** and then pure trans isomer **1b** (2.6 g), nmr δ 4.16 (q, 2, $COOCH_2$–, J = 7 Hz).

In an alternative preparation of *trans*-hydroxy ester **1b**, a mixture of *trans*-2-hydroxycyclopentanecarbonitrile[19] (18 g) and 150 ml of 15% aqueous KOH was refluxed during 4 hr, cooled, washed with ether, acidified with 10% HCl, and extracted with ether. The ether solution was dried and evaporated *in vacuo*, and the residue was dissolved in absolute ethanol (150 ml) saturated with hydrogen chloride. After 5-hr reflux the solvent was distilled *in vacuo* and water was added and the mixture was extracted with ether. The residue left after evaporation of the solvent was chromatographed as shown above to give 8.2 g of **1b**.

Grignard Reactions of Hydroxy Esters 1a and 1b. General Procedure.—A solution of the hydroxy ester (10 mmol) in 100 ml of dry ether was added dropwise under nitrogen to the ice-cooled solution of the Grignard reagent (PhMgBr or MeMgJ, 80 mmol in 100 ml of dry ether). The mixture was stirred (4 hr for PhMgBr and overnight for MeMgJ) at room temperature, then hydrolized with excess of NH_4C solution, the organic layer was separated, and the aqueous phase was extracted several times with ether. The combined ether layers were washed (aqueous NaCl solution) and dried (Na_2SO_4), the solvent was evaporated *in vacuo*, and the residue was chromatographed.

The *cis*-hydroxy ester **1a** afforded by the above procedure the diols **24a**[20] (71% yield, elution with hexane and 10% ether) and **27a** (73% yield, elution with pentane and 20% ether), respectively.

In the reaction of hydroxy ester **1b** and MeMgJ about 70% of the material was not recovered by extraction. Chromatography of the residue gave a low yield (11%) of diol **27b** (elution with pentane and 30% ether).

The residue (2 g) from the reaction of **1b** and PhMgBr was chromatographed on silica by the dry column method and afforded 0.52 g of 1-benzoylcyclopentene (23% yield, elution with pentane and 5% ether), varying amounts of α-methylbenzyl alcohol (0.1–0.4 g, pentane and 10% ether), *cis*-2-benzoylcyclopentanol (**20a**, 0.35 g, 14% yield, elution with pentane and 30% ether), *trans*-2-(α-hydroxybenzhydryl)cyclopentanol (**24b**, 0.16 g, 5% yield), and *trans*-2-benzoylcyclopentanol (**20b**, 0.64 g, 26% yield, pentane and 40% ether). The separation of **24b** and **20b** was completed by repeated chromatography, using as eluents 20% benzene and 80% methylene chloride. 1-Benzoylcyclopentene had bp 92° (0.5 mm), n^{25}D 1.564, nmr δ 6.53 (m, 1, $w_{1/2}$ = 5 Hz), uv max (EtOH) 251 nm (ϵ 16100), ir ($CHCl_3$) 1680 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.52; H, 7.21.

The previously reported reactions[21] of *cis*- and *trans*-2-hydroxycyclohexanecarboxylic esters with PhMgBr and MeMgI were repeated (in conditions shown for **1a** and **1b**) to determine and compare the yields of diols obtained from both stereoisomers. *cis*-2-(α-Hydroxybenzyhydryl)cyclohexanol (**28a**) and *cis*-2-(α-hydroxyisopropyl)cyclohexanol were obtained in 42 and 64% yields, respectively (after chromatographic purification), whereas the corresponding trans isomers (**28b** and **31b**) were formed in 82 and 84% yields.

Preparation of Hydroxy Ketones 2, 3, and 7 (Table I).—The diol (10 mmol) was dissolved in acetone (25 ml for diols **27a** and **31b**) and 75 ml for **24a**) and 2.5 ml of Jones reagent was added dropwise to the cooled solution (5°). After stirring for 5 min the mixture was diluted with water and extracted with chloroform. The organic layer was washed (CO_3HNa and NaCl solutions), dried, and evaporated *in vacuo*.

Diol **24a** (2.68 g) afforded 1.70 g (64%) of 2-(α-hydroxybenzhydryl)cyclopentanone (**2**), mp 165° (from chloroform and hexane).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.42; H, 6.78.

Diol **27a** (1.44 g) afforded, after chromatographic purification, 0.87 g (61%) of 2-(α-hydroxyisopropyl)cyclopentanone (**3**): bp 50–52° (0.3 mm); n^{20}D 1.458; nmr δ 1.19 (s, 3, CH_3), 1.41 (s, 3, CH_3).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.52; H, 10.12.

Diol **28b** (2.8 g) yielded 2.1 g (75%) of 2-(α-hydroxybenzydryl)-cyclohexanone (**7**), mp 174° (from chloroform and hexane).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.18. Found: C, 81.25; H, 7.05.

2-(α-Hydroxybenzyl)cyclopentanone (4) was prepared by the method reported[22] for the six-membered-ring homolog. The unreacted cyclohexanone and benzaldehyde were eliminated by distillation *in vacuo* and the part of the residue which was soluble in ether was chromatographed by the dry column method. Compound **4** was obtained by elution with pentane and 5% ether, in 16% yield, mp 60–61°, (from hexane), nmr δ 5.25 (d, 1, CHOH, J = 3 Hz), ir ($CHCl_3$) 1735 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: 75.92; H, 7.48.

The diastereomer of **4** (δ 4.72, d, 1) was also present in the reaction mixture but was not isolated pure.

2-Benzhydrylcyclopentanone (6).—A solution of hydroxy ketone **2** (0.78 g) in 50 ml of benzene and 100 mg of *p*-toluenesulfonic acid were refluxed for 1 hr. The resulting yellow solution was washed (aqueous CO_3HNa solution and water), dried, and evaporated *in vacuo*. 2-Benzylhydrylidenecyclopentanone had mp 116–117° (from hexane).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.31; H, 6.61.

The above compound (0.6 g) in 20 ml of methanol was hydrogenated over palladium on carbon powder. After absorption of the calculated volume of gas, the catalyst was removed by filtration and the solvent was evaporated. Chromatography of the residue (elution with pentane and 5% ether) afforded 0.42 g of **6**, mp 91–92° (from ether and pentane), nmr δ 4.64 (d, 1, Ph_2CH–, J = 5 Hz), ir ($CHCl_3$) 1736 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.12; H, 7.31.

***cis*- and *trans*-2-Benzoylcyclopentanols (20a and 20b).**—The reported[19] 2-hydroxycyclopentanenenitrile consisted of a stereoisomeric mixture which was separated by chromatography into trans isomer (72% of the total, elution with 1:1 pentane–ether) and cis isomer (28%, 1:2 pentane–ether). The trans configuration of the main isomer was verified as follows. A solution of the compound (0.5 g) in 10 ml of ethanol saturated with hydrogen chloride was kept at 10° for 48 hr. Evaporation of the solvent *in vacuo*, warming of the residue with 10 ml of water on a water bath during 30 min, and extraction with ether afforded the *trans*-hydroxy ester **1b** (0.32 g). The *cis*-hydroxy nitrile did not react in the above conditions.

To an ice-cooled solution of PhMgBr (from 10 g of PhBr) in 70 ml of dry ether was added a solution of 2-*cis*-hydroxycyclopentanenitrile[23] (1 g) in 25 ml of benzene and the reaction was continued at roon temperature for 3 hr. Hydrolysis and extraction (as shown for Grignard reactions of esters) yielded a residue which was stirred for 45 min at room temperature with a mixture of 10% AcOH (10 ml) and 10% HCl (10 ml). Water was then added and the mixture was extracted twice with ether. The combined ether layers were washed with aqueous solutions of Na_2CO_3 and NaCl, dried, and evaporated to give a residue which was chromatographed on a silica "dry" column affording at first *cis*-2-benzoylcyclopentanol (**20a**, 130 mg, elution with pentane and 30% ether): bp 102° (0.15 mm); n^{21}D 1.556; nmr δ 3.60 (m, 1, COCH–), 4.62 (br, 1, CHOH, $w_{1/2}$ = 6 Hz); ir ($CHCl_3$) 1671 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.62; H, 7.38.

trans-**2-Benzoylcyclopentanol (20b**, 255 mg) was eluted next with pentane and 40% ether: nmr δ 3.70 (m, 1, COCH–), 4.56 (br, 1, CHOH, $w_{1/2}$ = 8 Hz); ir ($CHCl_3$) 1676 cm^{-1}. The oil decomposed when distilled under reduced pressure and was characterized as the *p*-nitrobenzoate, mp 107° (crystallized from pentane and ether).

Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.42; H, 5.12, N, 3.92.

***cis*- and *trans*-2-Acetylcyclopentanols (21a and 21b).**—The *cis*-hydroxy nitrile (3 g) was treated with MeMgBr in conditions

(19) M. Mousseron, J. Julien, and F. Winternitz, *Bull. Soc. Chim. Fr.*, 878 (1948).

(20) All diols were obtained also from the corresponding hydroxy ketones (Table II). Data for new compounds are given in Table IV.

(21) H. E. Zimmerman and J. E. English, *J. Amer. Chem. Soc.*, **75**, 2367 (1953).

(22) D. Vorländer and K. Kunze, *Ber.*, **59**, 2079 (1926).

(23) The use of an isomeric mixture of 2-hydroxy nitriles lowered the reaction yields of this reaction.

TABLE IV

DATA ON THE PRODUCTS OF GRIGNARD REACTIONS

Compd[a]	Mp or bp (mm), °C	Nmr, δ (ppm)	Compd[a]	Mp or bp (mm), °C	Nmr, δ (ppm)
11	116–117[b]	0.95 (s, 3, CH_3)	**24a**	112–114[c]	4.29 (br, 1, CHOH, $w_{1/2}$ = 8 Hz)
12	105–106[c]	0.81 (s, 3, CH_3), 1.15 (s, 3, CH_3)	**24b**	119–120[c]	4.23 (br, 1, CHOH, $w_{1/2}$ = 10 Hz)
13	100–101[b,d]	1.41 (s, 3, CH_3), 5.15 (s, 1, PhCH, $w_{1/2}$ = 3Hz)	**25a**	79–80[e]	1.70 (s, 3, CH_3), 4.64 (br, 1, CHOH, $w_{1/2}$ = 6 Hz)
14	79–80[b]	3.64 (br, 2, CH_2OH)	**25b**	102–104[c,d]	1.59 (s, 3, CH_3), 3.97 (br, 1, CHOH, $w_{1/2}$ = 9 Hz)
15a	148–150 (0.25), $n^{20}D$ 1.566	0.77 (s, 3, CH_3), 4.04 (d, 1, PhCH, J = 11 Hz)	**26a**	130–132 (0.5), $n^{20}D$ 1.534	1.38 (s, 3, CH_3), 3.77 (br, 1, CHOH $w_{1/2}$ = 6 Hz)
15b	96–97[b]	1.20 (s, 3, CH_3), 3.72 (d, 1, PhCH, J = 12 Hz)	**26b**	80–81[b]	1.56 (s, 3, CH_3), 4.15 (br, 1, CHOH, $w_{1/2}$ = 9 Hz)
16	128–129[b]	0.74 (s, 3, CH_3)	**27a**	44–45[e]	1.19 (s, 3, CH_3), 1.40 (s, 3, CH_3), 4.47 (br, 1, CHOH, $w_{1/2}$ = 6 Hz)
17	115–116[b]	0.65 (s, 3, CH_3), 1.13 (s, 3, CH_3)	**27b**	83[b,d]	1.17 (s, 3, CH_3), 1.21 (s, 3, CH_3), 4.14 (br, 1, CHOH, $w_{1/2}$ = 9 Hz)
18	117[b]	1.47 (s, 3, CH_3), 5.43 (s, 1, PhCH, $w_{1/2}$ = 3 Hz)	**29a**	166–168[f]	1.67 (s, 3, CH_3), 4.62 (br, 1, CHOH, $w_{1/2}$ = 6 Hz)
19a	97[b]	0.99 (d, 3, CH_3, J = 7 Hz)	**29b**	128[c]	1.57 (s, 3, CH_3), 3.11 (br, 1, CHOH, $w_{1/2}$ = 13 Hz)
19b	130–132 (0.1), $n^{24}D$ 1.545	0.78 (d, 3, CH_3, J = 7 Hz)	**30b**	108–109[c]	1.61 (s, 3, CH_3), 3.72 (br, 1, CHOH, $w_{1/2}$ = 14 Hz)

[a] Satisfactory analytical data (±0.3%) were obtained for all compounds reported in the table: Ed. [b] Crystallized from pentane and ether. [c] Crystallized from hexane and chloroform. [d] Because of distillation difficulties the oily diol was characterized (melting point and elementary analysis) as the secondary mono-*p*-nitrobenzoate. [e] Crystallized from cold pentane. [f] Crystallized from ethanol.

shown for the preparation of **20a** and **20b**. The reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and stirred with it for 2 hr at room temperature. The organic layer was separated and the aqueous layer was extracted with ether. Work-up and chromatography as shown previously yielded at first **21a** (0.22 g, elution with pentane and 30% ether): bp 85–88° (1.5 mm); $n^{18}D$ 1.468; nmr δ 2.23 (s, 3, CH_3), 4.52 (br, 1, CHOH, $w_{1/2}$ = 7 Hz); ir ($CHCl_3$) 1706 cm^{-1}.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.76; H, 9.40.

After a few fractions containing a mixture of **21a** and **21b** (0.28 g), the pure trans isomer **21b** (0.52 g) was obtained: bp 86–88° (1.5 mm); $n^{19}D$ 1.465; nmr δ 2.22 (s, 3, CH_3), 4.40 (br, 1, CHOH, $w_{1/2}$ = 13 Hz); ir ($CHCl_3$) 1710 cm^{-1}.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.72; H, 9.32.

Preparation of 2-Acylcyclohexanols (22a, 22b, and 23).—The reported[19] *trans*-2-hydroxycyclohexanecarbonitrile was found to consist of 90% trans isomer and 10% cis isomer. The isomers were separated as shown for the hydroxy nitriles in the cyclopentane series. The trans isomer (5 g) was treated with MeMgBr by the procedure used for the preparation of **21a** and **21b**. The product was purified by chromatography on silica (elution with pentane and 30% ether) to yield 3.2 g of *trans*-2-acetylcyclohexanol (**23**): bp 73–75° (0.8 mm); $n^{24}D$ 1.472; nmr δ 2.22 (s, 3, CH_3), 3.83 (br, 1, CHOH, $w_{1/2}$ = 14 Hz); ir ($CHCl_3$) 1700 cm^{-1}.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: 67.73; H, 10.02.

The reaction of *trans*-hydroxycyclohexanecarbonitrile (5.8 g) with an excess of PhMgBr was carried out under conditions given for **20a** and **20b** and afforded *trans*-2-benzoylcyclohexanol (**22b**, 2.8 g): mp 81–82° (from chloroform and hexane); nmr δ 3.38 (br, 1, COCH), 4.03 (m, 1, CHOH, $w_{1/2}$ = 21 Hz); ir ($CHCl_3$) 1672 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.28; H, 7.82.

The reaction of *cis*-2-hydroxycyclohexanenitrile (1 g) with PhMgBr was carried out under the same conditions except that longer exposure to acid (2 hr) was needed for the hydrolysis of the imine. *cis*-Benzoylcyclohexanol (**22a**, 0.46 g) had mp 72–73° (from ether and pentane); nmr δ 3.37 (m, 1, COCH), 4.27 (m, 1, CHOH, $w_{1/2}$ = 8 Hz); ir ($CHCl_3$) 1676 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: 76.18; H, 7.96.

Grignard Reactions of Compounds 2–10 and 20–23. General Procedure.—A solution of 10 mmol of ketone in 100 ml of dry ether (except the less soluble ketones **2** and **7**, which were dissolved in 200 ml of benzene) was added dropwise under nitrogen to an ice-cooled solution of 60 mmol of Grignard reagent in 100 ml of ether. Ketones **20a** and **22b** were preferably added at 18°. The reaction mixtures were stirred at room temperature for 4 hr (except compound **2** which was allowed to react overnight), decomposed by an excess of saturated NH_4Cl solution, and extracted with ether in the manner shown for Grignard reactions of hydroxy esters. The crude reaction mixtures were analyzed by tlc, ir, and nmr spectroscopy and then chromatographed on silica (dry column method) using pentane and ether as eluent mixture. The identical diol fractions (tlc) were combined and other fractions were also submitted to tlc and nmr analysis to determine if an isomeric diol was present. Data on newly prepared diols are given in Table IV.

The reaction of hydroxy ketone **10** (1 g, isomeric mixture) with PhMgBr in the above conditions yielded a mixture of diols which was partly separated by chromatography on silica (elution with pentane and 20% ether): diol **19a** (65 mg) was followed by several fractions containing both isomers (327 mg) and by the pure diol **19b** (480 mg). Both diols were separately submitted to Jones oxidation by addition of the reagent (0.1 ml) to the diol (60 mg) in acetone solution (3 ml) at 10°, under nitrogen. Addition of water (after 3-min stirring) and extraction with ether afforded in both cases, after chromatography (elution with pentane and 15% ether), 1-phenyl-*c*-2-acetyl-*r*-1-cyclopentanol (35 mg): mp 67° (from cold pentane); nmr δ 1.88 (s, 3, CH_3), 3.14 (t, 1, COCH); ir ($CHCl_3$) 1700 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 77.03; H, 8.31. Found: C, 76.83; H, 8.26.

The reactions of compound **20b** with MeMgBr yielded, in addition to diols **25b** and **26b**, also some 1-benzoylcyclopentene and starting material. The reaction of **20b** with PhMgBr gave results very similar to those obtained in the reaction of the *trans*-hydroxy ester **1b** and PhMgBr.

Jones oxidation of Diols 25a, 25b, 26a and 26b.—The corresponding diol (200 mg) was dissolved in 5 ml of pure acetone and treated with Jones reagent (0.25 ml) as described previously. Work-up and chromatographic purification (elution with 20–30% ether and pentane) afforded 110–120 mg (about 60% yield) of the hydroxy ketone. Some starting material was recovered from the column after the product was eluted. Diols **25a** and **25b** afforded by the above oxidation the same hydroxy ketone (2*RR*,2α*SS*)-2-(α-hydroxy-α-methyl)benzylcyclopentanone, mp 70–71° (from pentane and ether), nmr δ 1.72 (s, 3, CH_3), ir ($CHCl_3$) 1726 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.29; H, 7.82.

Diols **26a** and **26b** afforded (2*RS*,2α*SR*)-2-(α-hydroxy-α-methyl)benzylcyclopentanone, bp 85–87° (0.25 mm), $n^{20}D$ 1.535, nmr δ 1.58 (s, 3, CH_3), ir ($CHCl_3$) 1724 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.42; H, 7.78.

Separate oxidations of diols **29a** and **29b** by the same manner provided (2*RR*,2α*SS*)-2-(α-hydroxy-α-methyl)benzylcyclohexanone, bp 88–90° (0.4 mm), $n^{25}D$ 1.524; nmr δ 1.64 (s, 3, CH_3), ir ($CHCl_3$) 1698 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.85; H, 8.36.

Deuteration of *trans*-2-Benzoylcyclopentanol (20b).—A solution of **20b** (0.6 g) in dimethoxyethane (10 ml), D_2O (3 ml), and 40 mg of anhydrous Na_2CO_3 were refluxed for 16 hr. Extraction with ether and chromatography of the residue on a dry column afforded 0.32 g of 2-d_1-*trans*-2-benzoylcyclopentanol which was eluted with 40% ether and pentane. Nmr showed no chemical shift in the δ 3.5–4.0 region, mol wt 191 (mass spectrum).

Grignard reaction of deuteriated **20b** (0.3 g) with PhMgBr by the usual procedure yielded, along with other products, **20a** (30 mg) and **20b** (65 mg) which were separated by dry column chromatography as shown for the reaction of **1b** and PhMgBr. The exchange of deuterium on hydrogen was proven by nmr analysis and by mass spectral determination of molecular weight of **20a** and **20b** (190).

Registry No.—**2**, 32338-46-8; **3**, 32338-48-0; **4**, 32338-47-9; **6**, 30614-37-0; **7**, 33831-21-9; **11**, 33831-22-0; **12**, 33831-23-1; **13** *p*-nitrobenzoate, 33847-00-6; **14**, 33831-24-2; **15a**, 33831-25-3; **15b**, 33831-26-4; **16**, 33831-27-5; **17**, 33831-28-6; **18**, 33831-29-7; **19a**, 33872-39-8; **19b**, 33831-30-0; **20a**, 32346-66-0; **20b** *p*-nitrobenzoate, 33831-32-2; **21a**, 32435-36-2; **21b**, 33830-23-8; **22a**, 33830-24-9; **22b**, 33830-25-0; *trans*-**23**, 33830-26-1; **24a**, 33830-27-2; **24b**, 33830-28-3; **25a**, 33830-29-4; **25b** *p*-nitrobenzoate, 33847-01-7; **26a**, 33830-30-7; **26b**, 33830-31-8; **27a**, 33830-32-9; **27b** *p*-nitrobenzoate, 33847-02-8; **29a**, 33872-40-1; **29b**, 33830-33-0; **30b**, 33830-34-1; 1-benzocyclopentene, 21573-70-6; 2-benzylhydrylidenecyclopentanone, 14636-29-4; 1-phenyl-*c*-2-acetyl-*r*-1-cyclopentanol, 33830-37-4; (2*RR*,2α*SS*)-2-(α-hydroxy-α-methyl)benzylcyclopentanone, 33830-38-5; (2*RS*,2α*SR*)-2-(α-hydroxy-α-methyl)benzylcyclopentanone, 33830-39-6; (2*RR*,2α*SS*)-2-(α-hydroxy-9-methyl)benzylcyclohexanone, 33830-40-9.

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Acid-Catalyzed Rearrangement of 6-Methyltricyclo[4.4.0.0^{2,7}]decan-3-one

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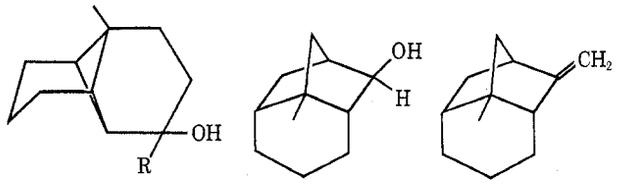
Tricyclic ketone **5** reacts in concentrated sulfuric acid to give rearrangement products **6**, **7**, **8**, and **9** in a ratio of 19:32:10:38. Tricyclic ketone **6** is produced by a mechanism involving ring expansion while compounds **7**–**9** arise by a route involving initial ring opening of ketone **5**. The structures of the rearrangement products were rigorously defined.

In the previous paper,[1] we reported that tricyclic alcohols **1** and **2** rearrange in the heterogeneous medium hexane–50% aqueous sulfuric acid to yield compounds **3** and **4**, respectively. In this paper, we describe the

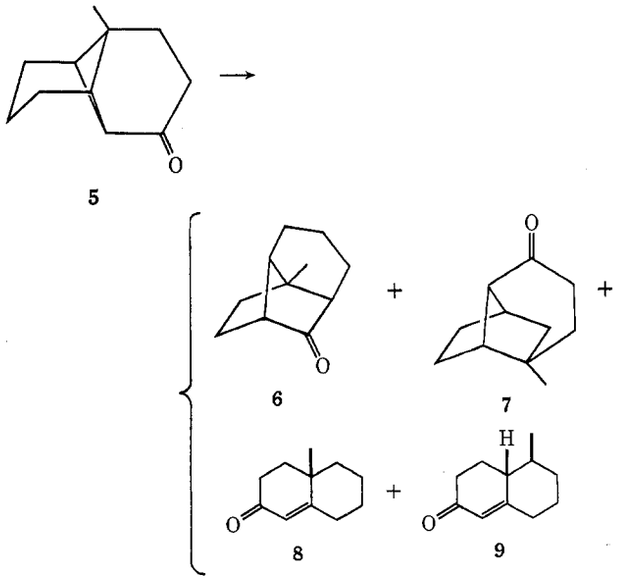


1, R = H
2, R = CH_3
3
4

acid-catalyzed rearrangement of the parent tricyclic ketone, 6-methyltricyclo[4.4.0.0^{2,7}]decan-3-one (**5**).

When ketone **5** is dissolved in concentrated sulfuric acid and the resulting solution kept at room temperature for periods ranging from 2 hr to 2 weeks, four isomeric ketones are produced. These isomeric products, subsequently shown to have structures **6**–**9** (*vide infra*), were each isolated in a pure state by a combination of column chromatography and preparative glpc. The product analyses from several such runs are tabulated in Table I. Control experiments showed that none of the products react further when treated with concentrated sulfuric acid at 25° for 2 days.

The structures of the four products were assigned on



the following grounds. Ketone **8** is a known compound and was identified by comparison with an authentic specimen.[2]

Product **9** also exhibits spectral properties characteristic of an α,β-unsaturated ketone [ν_{max} 1680 and 1629 cm^{-1}, λ_{max} 238 nm (ε 12,200)]. The pmr spectrum

(1) B. E. Ratcliffe and C. H. Heathcock, *J. Org. Chem.*, **37**, 531 (1972).

(2) J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964), and references cited therein.