4.43 μ (C-D str); nmr ($CDCl_3$), δ 7.32 (d, J = 15.5 Hz, 1.02), 6.18 (d, J = 15.5 Hz, 1.00), and 3.78 (s, 6)

Registry No.—Methanol, 67-56-1; **1b**, 17038-07-2; **2a**, 17037-89-7; **2b** (R_3 = C_2H_5), 17037-90-0; **2b** (R_3 = CH_3), 17037-91-1; **2c**, 3402-60-6; **3**, 17038-08-3; **4**, 17037-93-3; 4,4-dimethylcyclopentane-1,3-dione-2-carboxylic acid, 17037-94-4; **5**, 17037-95-5; **7**, 17037-97-7; **8**, 17037-96-6; **9**, 17038-09-4; **10**, 17038-10-7; **11**, 17037-98-8; **14**, 5921-03-9; **15**, 17038-00-5; **16**, 17038-01-6; **17**, 17038-02-7; **18**, 17038-03-8; **19**, 17038-04-9; **20**, 17038-05-0; **22**, 17038-06-1.

Acknowledgment.—We thank Miss V. Parmakovich, Columbia University, for determining the mass spectra. We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

The Synthesis and Stereochemical Assignment of *cis*- and *trans*-2-Methyl-2-pentenoic Acid and the Corresponding Esters, Aldehydes, and Alcohols[1a]

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Received March 7, 1968

The title compounds were prepared by standard procedures. The *trans* acid, ester, and alcohol are distinguished from the corresponding *cis* isomers in the nmr spectrum by the chemical shift of the β-vinyl proton which lies at lower field by 0.82, 0.82, and 0.10 ppm, respectively, in $CDCl_3$. In the aldehydes, however, the β-vinyl proton signals are separated by only 0.01 ppm and cannot be used to distinguish the isomers. Differentiation can be made *via* the aldehydic proton signal which lies 0.73 ppm downfield in the *cis* isomer. The difference in chemical shift of the β-vinyl protons increases to 0.98, 1.08, and 0.15 ppm in C_6D_6 for the acid, ester, and alcohol, respectively, but remains essentially unchanged in the aldehydes. Solvent shifts, $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$, were calculated and found useful for the stereochemical assignment of the acids and esters but not for the aldehydes and alcohols for which one must rely upon the chemical shift of the appropriate protons.

Several methods for assigning the stereochemistry of *cis–trans* carbon–carbon double-bond isomers are available.[2] Of these the application of nmr spectroscopy is well suited to the problem of trisubstituted ethylenes and has been applied with respect to isoprenoids of the type alkyl-$CH_2(CH_3)C{=}CH(CH_2OH)$,[3a] $-(CHO)$,[3b] $-(COOCH_3)$.[3c] On the other hand, there are an increasing number of diversified[4] natural products containing the partial structure $RCH{=}C(CH_3)R'$ where R = dialkyl $-CH-$ or most often alkyl $-CH_2-$ and R' = CH_2OH,[4] CHO,[5] COOH,[6] and $COOCH_3$.[7] Although studies have been made for the acids and esters,[8] no model compound studies of the application of nmr spectra to the stereochemistry of such aldehydes and alcohols have been reported.

We therefore decided to synthesize the *cis* and *trans* isomers of 2-methyl-2-penten-1-ol since they would serve as models for a number of sesquiterpene alcohols recently characterized.[4b,9] In addition, these isomers would have the advantage[10] of being homologs of angelic and tiglic acid. Preparation of the corresponding aldehydes was also desirable since the assignment of their stereochemistry is not well documented.[11] The acids and esters were also prepared for comparison with previous studies and thus provide an additional basis for the assignment of stereochemistry to the aldehydes and alcohols.

Synthesis.—The synthesis of any one pair of isomers would afford the other pairs of isomers by standard transformations. Since the synthesis and separation of the isomeric acids had been reported,[12] these were the starting materials for the syntheses outlined in Scheme I. Hydrolysis of 2-pentanone cyanohydrin yielded the expected 2-hydroxy-2-methylpentanoic acid (**1**). Pyrolysis of **1** afforded a product from which the isomerically pure (*E*)-2-methyl-2-pentenoic acid[13] (**2**) was obtained after spinning-band distillation. However, the fraction containing the *cis* isomer, (*Z*)-2-methyl-2-pentenoic acid (**3**), was contaminated with an impurity exhibiting nmr vinyl proton signals at δ 5.61 (q, $J \sim 1.5$ Hz) and 6.28 (d, $J \sim 1.5$ Hz)[14] which is consistent with the formation of 2-methylene-

(1) (a) Supported in part by the National Science Foundation. (b) On leave from the Department of Chemistry, University of Malaya, Kuala Lumpur.

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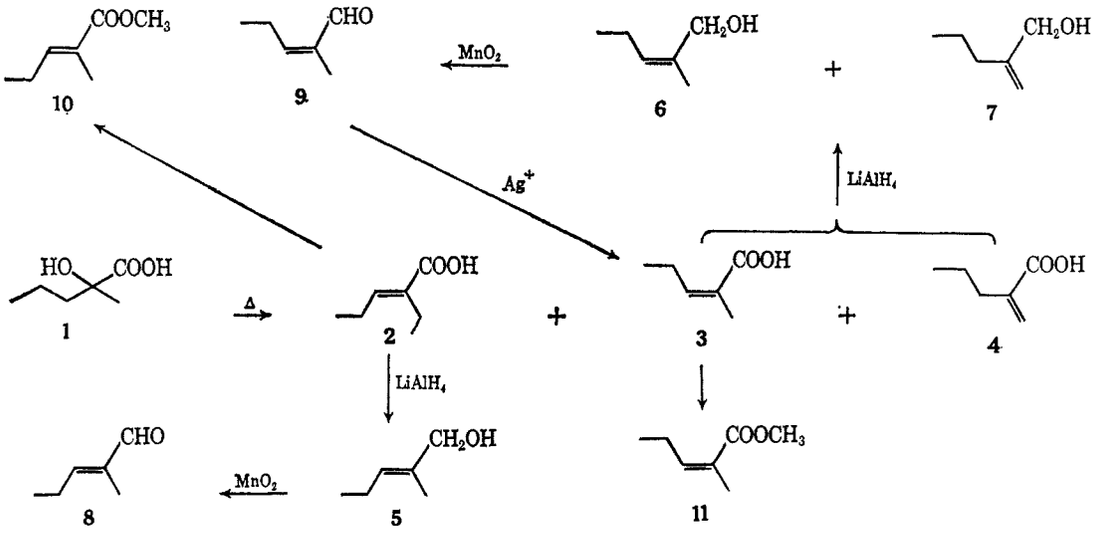
SCHEME I



pentanoic acid (**4**).[15] Extending the reaction time from 1 to 5 hr at ~245° (bath) changes the ratio of isomers from 4:3:4 to 1:3:4 for **3**, **2**, and **4**, respectively, as determined by nmr spectroscopy. Thus the formation of **4** could not be avoided by extended reaction time.

Since distillation would not separate the *cis*- (**3**) and α-methylene (**4**) acids nor the corresponding mixture of alcohols, **6** and **7**, respectively, silver nitrate treated silica gel tlc was employed on (a) a mixture of the methyl esters of **3** and **4**, (b) the alcohols **6** and **7**, and (c) the corresponding acetates. Only the alcohols showed two spots[16] and were subsequently separated by column chromatography to yield the tlc pure *cis* isomer, (*Z*)-2-methyl-2-penten-1-ol (**6**). The chromatography was unique since the *cis* alcohol could be eluted with complete retention of the methylene compound **7** on the column. The remainder of the isomerically pure *cis* series of compounds was obtained by successive oxidation of the alcohol **6** and the aldehyde **9** to the acid **3** which in turn gave the corresponding ester **11**. In an analogous manner the *trans* acid **2** afforded the remaining stereochemically pure alcohol **5**, aldehyde **8**, and ester **10**.

Stereochemistry.—The β-vinyl proton is more sensitive to environmental changes[8] than other protons and is thus preferred for stereochemical assignments. The values determined for the isomeric acids and esters[17] in $CDCl_3$ are in accord with previously published data[8] and thus form a sound basis for the assignment of the stereochemistry of the alcohols and aldehydes. Since no isomerization was observed in the formation of the latter, the products retained the stereochemistry of the respective acid. The difference in the position of the β-vinyl proton in the isomeric alcohols is much smaller than in the acids and esters but sufficiently large for configurational assignment, providing that the vinyl proton is not affected significantly by neighboring groups in the molecule. The differences in chemical shift of the vinyl methyl and carbinol protons are slightly larger and therefore will also be of value in determining the stereochemistry of the isomeric alcohols.

Unexpectedly, the vinyl proton signal in the isomeric aldehydes shows essentially no difference in chemical shift (0.01 ppm) and cannot be used to assign stereochemistry.[18] However, the aldehydic proton shows a difference[9a] in chemical shift similar to that shown by the vinyl proton of the acids and esters, the *cis* aldehyde (**9**) exhibiting its signal at 0.73 ppm lower field than the *trans* isomer (**8**). Consequently, the position of the *aldehydic proton* may be used to distinguish *cis* and *trans* isomers.[19] In addition, differences in chemical shift of the methylene protons of the acids, esters, aldehydes, and alcohols in $CDCl_3$ are 0.34, 0.27, 0.17, and 0.03 ppm, respectively. Contrary to its other unexpected behavior, the aldehyde now follows the pattern of the acids and esters to provide an additional, though less pronounced, structural feature for assigning stereochemistry.

It should be pointed out that the *cis* aldehyde (**9**) is unstable and easily isomerizes[20] to the *trans* aldehyde (**8**). For example, after 48 hr, nmr spectroscopy indicated about 35% **8** in a sample of **9** which initially was free of the *trans* isomer (**8**). Likewise glpc[21] of the *cis* aldehyde yielded a mixture of similar composition.

(15) This isomer was not detected previously[12] since only the lower boiling fraction (*trans*) and intermediate fractions (~1:1 *cis*–*trans*) were ozonized to give 60% propionaldehyde without detection of any formaldehyde.

(16) Silver nitrate–Kiesel gel (1:4, w/w) with elution according to E. Stahl and H. Vollmann, *Talanta*, **12**, 525 (1965), produced R_F 0.62 (**6**) and 0.49 (**7**).

(17) D. E. McGreer, P. Morris, and G. Carmichael, *Can. J. Chem.*, **41**, 726 (1963); D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *ibid.*, **43**, 1407 (1965).

(18) The chemical shifts of the β-vinyl proton in the aldehydes reported by G. Büchi and H. Wüest, *Helv. Chim. Acta*, **50**, 2440 (1967), do not bear upon the proof of configuration. The assignment of *trans* stereochemistry to the α,β-unsaturated aldehydes was based upon the stereospecific transformation of the aldehydes to the corresponding acid and ester and the chemical shifts of their β-vinyl proton compared with those of tiglic and angelic acid and methyl ester.

(19) The doubling of the vinyl methyl and vinyl proton signals and the values for δ 10.2 and 9.3 for the aldehydic proton reported for vallesiachotamine by C. Djerassi, H. J. Monteiro, A. Walser, and L. J. Durham, *J. Amer. Chem. Soc.*, **88**, 1792 (1966), may also be interpreted as being due to a mixture of *cis* and *trans* isomers which may or may not occur naturally; *cf.* footnote 20 and related discussion.

NOTE ADDED IN PROOF.—The nmr signal at δ 9.3 reported by F. Bohlmann and C. Zdero, *Tetrahedron Lett.*, 1533 (1968), for (−)-α-santalal is not in accord with the indicated stereochemistry of the *cis*-α,β-unsaturated aldehyde, for which δ ~10.2 would be expected.

(20) (a) K. Saskai, *Nippon Kagaku Zasshi*, **87**, 763 (1966), reports that the oxidation of either geraniol or nerol with *t*-butyl chromate yields a mixture of citral a and b. (b) The isolation of α- and β-sinensal with *trans*-α,β-unsaturated aldehydes raises the question of whether or not they may have existed originally as the *cis* isomer.

(21) 10% SE-30 column at 25° with injector at 75°.

TABLE I

NMR ABSORPTIONS[a] (δ) OF ISOMERIC ACIDS, ESTERS, ALCOHOLS, AND ALDEHYDES IN CHLOROFORM AND BENZENE

	In $CDCl_3$					In C_6D_6				
Compound	CH_3[b]	CH_2[c]	HC=[d]	$=C(CH_3)$[e]	Other[f]	CH_3[b]	CH_2[c]	HC=[d]	$=C(CH_3)$[e]	Other
trans acid **2**	1.06	2.22	6.88	1.81		0.78	1.88	6.87	1.73	
cis acid **3**	1.03	2.56	6.06	1.89		0.93	2.50	5.89	1.80	
trans alcohol **5**	0.95	2.04	5.35	1.63	3.92	0.92	1.98	5.35	1.57	3.87
cis alcohol **6**	0.95	2.07	5.25	1.78	4.08	0.90	2.02	5.20	1.77	4.04
trans aldehyde **8**	1.11	2.38	6.45	1.73	9.38	0.92	2.12	6.15	1.62	9.27
cis aldehyde **9**	1.10	2.55	6.46	1.72	10.11	0.87	2.25	6.12	1.62	9.99
trans ester **10**	1.04	2.18	6.72	1.82	3.71	0.87	1.97	6.73	1.87	3.52
cis ester **11**	1.01	2.45	5.90	1.88	3.71	0.90	2.44	5.65	1.78	3.42

[a] Spectra were measured on a Varian A-60 spectrometer using internal TMS ($\delta = 0$). [b] All signals appeared as quartets ($J = 7$ Hz). [c] All signals appeared as five-line multiplets ($J = 7$ Hz). [d] All signals appeared as a triplet ($J = 7$ Hz) of quartets ($J = \sim 1.0$ Hz). [e] All signals appeared as a five-line multiplet ($J = \sim 1.0$ Hz), except for **5** which exhibited a broadened singlet. [f] Except for OH; all signals appeared as singlets.

Presumably complete isomerization would occur under appropriate conditions.[22]

A recent attempt[23] has been made to calculate the chemical shift of the vinyl proton on a substituted ethylene by assigning substituent effects from measurements on a variety of compounds. Using a generalized alkyl group for the vinyl methyl and ethyl groups, a reasonable correlation with our data in $CDCl_3$ on the acids and esters was obtained, the calculated difference in chemical shift between isomers being 0.58 and 0.56 ppm, respectively. However, calculations gave essentially no difference (0.02 ppm) for the isomeric alcohols, while the vinyl proton of the *trans* aldehyde was predicted to lie at 0.27 ppm *lower field* than the *cis* aldehyde. This is not in accord with the absence of isomer effect observed and is also in the opposite direction anticipated from the normal deshielding of the carbonyl group.[3b] Thus the correlation does not extend to the isomeric alcohols and aldehydes.

To ascertain if the stereochemical assignments could be further characterized as has been done by solvent shifts in other systems,[24] the nmr spectra were also determined in C_6D_6. As can be seen from Table I, there is an increase in the difference of the chemical shift of the β-vinyl proton within each isomeric pair. This increase is primarily due to an upfield shift for the vinyl proton in the *cis* isomer except in the aldehydes where both isomers show the same upfield shift. Thus the difference between isomers can be enhanced by determining the nmr spectra in C_6D_6 for the acids, esters, and alcohols, but not for the aldehydes in which the difference increases to only 0.03 ppm. This same trend is also observed for the methylene protons in the acids and esters. However, the difference in chemical shift of the aldehyde methylene protons decreases while the same group in the alcohols shows no significant change.

Solvent shifts ($\Delta = \delta_{CCl_4} - \delta_{C_6H_6}$ ppm) were recently determined for a series of α,β-unsaturated acids and esters[24] in which it was found that the difference in solvent shift ($\Delta' = \Delta^t - \Delta^c$) for β protons or methyl groups on a single isomer ranged from 0.26 to 0.61 and could thus be used to determine the stereochemistry of one isomer without the presence of the other isomer for comparison. Our data for the acids and esters is in accord with this finding that the substituent *trans* to the functional group experiences a larger solvent shift than the *cis* substituent. The difference in solvent shift, $\Delta' = 0.22$–0.34 for the esters and *trans* acid, is in close agreement with the above values, the one exception being the *cis* acid which has $\Delta' = 0.11$.

The aldehydes, unexpectedly, show only $\Delta' = 0.04$, the sign being positive for the *cis* but negative for the *trans* isomer. Thus the applicability of the difference in solvent shift for assigning stereochemistry does not hold for the aldehydes. As might be expected also Δ' values for the alcohols are not significant. Thus one must rely upon the chemical shift of the appropriate protons for the assignment of the stereochemistry of the aldehydes and alcohols.

Experimental Section[25]

2-Hydroxy-2-methylpentanoic Acid (1).—A 150-g sample of 2-pentanone was converted according to the prescribed procedure[12] into 127 g (55%) of **1**: bp 78–83° (1 mm); mp 51–52° [lit.[12] bp 88–90° (1 mm); mp 50–52°]; nmr ($CDCl_3$), δ 0.90 (t, 3, $J = 7$ Hz, CH_3–CH_2), 1.45 (s, 3), 1.63 (m, 4), 7.85 (s, 2).

Pyrolysis of 1.—A 127-g sample of **1** was pyrolyzed[12] to afford 83.5 g (76%) of a mixture of acids **2**, **3**, and **4**: bp 215° (lit.[12] bp 220°); uv max (H_2O), 215 nm. Distillation of 99 g of the acid mixture through a spinning-band column (1 cm × 60 cm) gave 44 g (32%) of a mixture of the acids **3** and **4**, bp 98–108° (15 mm), 22 g (16%) of **(*E*)-2-methyl-2-pentenoic acid (2)**, bp 108–125° (15 mm) [lit.[12] bp 106.5° (10 mm)], and 30 g of **1**, bp 105–107° (3 mm). Recrystallization of **2** from methanol–water[12] afforded the analytical sample, mp 21.5–23° (lit.[12] mp 24.1°).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.4; H, 9.1.

The effect of heat on product distribution was studied by heating at 245° (bath) separate 2.9-g samples of **1**. Distillation at 285° (bath) after 1 hr gave 1.6 g of acids: bp 172–195°; the nmr ($CDCl_3$) data indicated **2**, **3**, and **4** to be present in the ratio of 3:4:4, respectively. After 5 hr, 1.8 g of acids was obtained: bp 170–210°; **2**, **3**, and **4** were present in the ratio of 3:1:4, respectively, by nmr spectroscopy ($CDCl_3$).

(*E*)-2-Methyl-2-penten-1-ol (5).—Using the procedure for reduction of phenylacetic acid,[26] 10 g of acid **2** afforded 5.3 g (60%) of alcohol **5**, bp 74–75° (20 mm) [lit.[27] bp 61–63° (14 mm)].

(22) (a) The oxidation[9d] of nuciferol (*cis*) to nuciferal (*trans*) with chromium trioxide in pyridine (and subsequent lithium aluminum hydride reduction of nuciferal to an alcohol isomeric with nuciferol) may proceed *via* the *cis* aldehyde; the isomerization of morellin (*cis* CHO at δ 9.63, $CDCl_3$) to isomorellin (*trans* CHO, δ 9.18) with KOH–ether is reported by G. Kartha, G. N. Ramachandran, H. B. Bhat, P. Madhavan Nair, V. K. N. Raghavan, and K. Venkataraman, *Tetrahedron Lett.*, 459 (1963). (b) The 2-methyl-2-pentenal, bp 130–140°, obtained by O. Doebner and A. Weissenborn, *Chem. Ber.*, **35**, 1143 (1902), from the self-condensation of propionaldehyde is confirmed by us (bp 135–138°) to be all *trans* (any *cis* isomer formed may have isomerized).

(23) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(24) J. Ronayne and D. H. Williams, *J. Chem. Soc., C*, 2642 (1967), and references therein.

(25) Analyses were performed by the Microchemical Laboratory, University of California at Berkeley.

(26) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 2548 (1947).

(27) A. Guillemonat, *Ann. Chim.* (Paris), **11**, 150 (1939), did not establish the stereochemistry, but it is assumed to be *trans*.

The analytical sample was obtained by short-path distillation.

Anal. Calcd for $C_6H_{12}O$: C, 71.9; H, 12.1. Found: C, 71.6; H, 11.9.

(*Z*)-2-Methyl-2-penten-1-ol (6).—Following the procedure for the preparation of alcohol **5**, 15 g of the acid mixture consisting of **3** and **4** gave 9.6 g (74%) of a mixture of the alcohols **6** and **7**, bp 71–74° (20 mm). The alcohols were separated by column chromatography on silver nitrate–alumina, prepared by adding 84 ml of saturated aqueous silver nitrate to 940 g of neutral alumina, activity I. The mixture was shaken vigorously until no lumps remained and allowed to stand for 48 hr; 9.7 g of the mixture of alcohols **6** and **7** was then applied. Elution with hexane–ether (1:4) yielded 7.7 g of alcohol **6** free of **7** by tlc.[16] Distillation afforded analytically pure **6**, bp 71–74° (15 mm).

Anal. Calcd for $C_6H_{12}O$: C, 71.9; H, 12.1. Found: C, 71.9; H, 12.5.

(*E*)-2-Methyl-2-pentenal (8).—To a solution of 1 g of alcohol **5** in 15 ml of methylene chloride was added 15 g of freshly prepared manganese dioxide.[28] After shaking for 18 hr at room temperature, the solid was filtered off and the solvent evaporated to give the crude aldehyde **8**. Short-path distillation gave 0.81 g (83%) of **8** as a slightly yellow, volatile liquid that decomposes with ease under nitrogen at 3°: see footnote 22b for boiling point data; uv max (95% EtOH), 228 nm (ϵ 12,000); ir ($CHCl_3$), 2730 (CHO), 1685 (C=O), 1645 (C=C).

Anal.[29] Calcd for $C_6H_{10}O$: C, 73.4; H, 10.3. Found: C, 72.4; H, 10.2.

(*Z*)-2-Methyl-2-pentenal (9).—Following the procedure for preparation of aldehyde **8**, 0.96 g of alcohol **6** in 60 ml of methylene chloride was oxidized with 15 g of manganese dioxide to afford 0.62 g (64%) of the aldehyde **9**. Spectroscopic data were determined on a freshly prepared sample: uv max (95% EtOH), 237 nm (ϵ 8900); ir ($CHCl_3$), 2743 (CHO), 1673 (C=O), 1656 (C=C). Short-path distillation under nitrogen followed by glpc[21] afforded the analytical sample which was isomerically pure.

Anal.[29] Calcd for $C_6H_{10}O$: C, 73.4; H, 10.3. Found: C, 71.3; H, 10.2.

(*Z*)-2-Methyl-2-pentenoic Acid (3).—A 4.0-g sample of the freshly prepared aldehyde **9** was oxidized in the described manner[30] to yield 3.26 g (70%) of the acid **3**, bp 102–103.5° (15 mm) [lit.[12] bp 94.0–94.4° (10 mm)].

Methyl (*E*)-2-Methyl-2-pentenoate (10).—To 0.8 g of acid **2** in 5 ml of methanol was added 0.1 ml of concentrated sulfuric acid. The mixture was refluxed for 1.5 hr and then poured into 15 ml of ice–water. The aqueous solution was extracted with three 10-ml portions of ether, and the combined ether extracts were washed twice with saturated sodium bicarbonate and then dried ($MgSO_4$). Evaporation of the solvent gave 0.62 g (69%) of the methyl ester **10**.[17] Short-path distillation gave the analytical sample.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.5; H, 9.3.

Methyl (*Z*)-2-Methyl-2-pentenoate (11).—A 0.9-g sample of acid **3** was esterified according to the procedure for the preparation of ester **10** to give 0.3 g (31%, 78% based upon the recovery of 0.56 g of **3**) of the methyl ester **11**.[17] Short-path distillation gave the analytical sample.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.3; H, 9.3.

Registry No.—**2**, 16957-70-3; **3**, 1617-37-4; **5**, 16958-19-3; **6**, 16958-20-6; **8**, 14250-96-5; **9**, 16958-22-8; **10**, 1567-14-2; **11**, 1567-13-1.

(28) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952), or O. Mancera, G. Rosenkranz, and F. Sondheimer, *ibid.*, 2189 (1953).

(29) These aldehydes are unstable and, though isomerically pure, repeatedly gave low carbon analyses.

(30) A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2343 (1928).

Diaxial Ring Opening of 1,2-Oxidocyclohexanes

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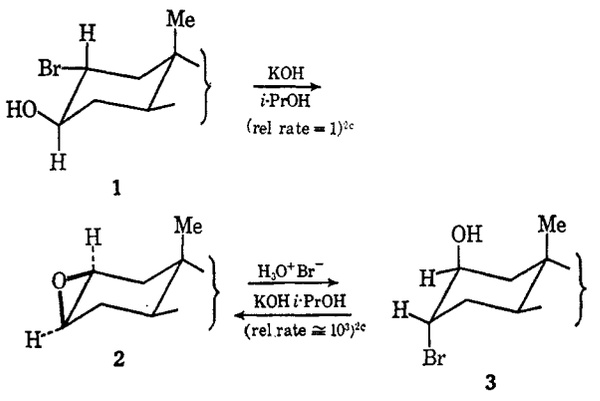
Received April 15, 1968

The synthetic sequence (2-bromo-4,4-diphenylcyclohexanone → bromohydrin → epoxide → new halohydrin → 2-halo-5,5-diphenylcyclohexanone) has been carried out in 42% over-all yield. The same sequence also has been applied successfully to 2-bromo-4-methyl-4-phenylcyclohexanone. These results show that one of two possible diaxial ring openings for 4,4-disubstituted 1,2-oxidocyclohexanes occurs stereoselectively.

In 2-halo keto steroids it is sometimes possible to interchange the positions of the halogen and carbonyl functions by the following sequence of steps: (1) hydride reduction, (2) conversion of the resulting halohydrin into an epoxide, (3) cleavage of the epoxide with a hydrohalogen acid to form a new halohydrin in which the positions of the halogen and hydroxyl functions have been interchanged, and (4) oxidation to regenerate the carbonyl function. For example, 2α-bromocholestan-3-one can be converted into 3α-bromocholestan-2-one in this way.[1] (This also serves as a means of converting cholestan-3-one into cholestan-2-one.[1])

The success of this method depends on a marked preference for diaxial ring closure in the formation of the epoxides and a marked preference for diaxial ring opening in the cleavage of epoxides.[1,2] Diaxial ring closure of 2α-bromocholestan-3β-ol (**1**) presumably proceeds *via* a boat conformation to form 2β,3β-oxidocholestane (**2**), which accounts for the 10^3 slower rate in this ring closure as compared to the formation of **2** by diaxial ring closure of 3α-bromocholestan-2β-ol (**3**).[2c] Hydrobromic acid cleaves **2** to give the diaxial bromohydrin **3**.[2b]



It was of interest to see whether 2-halo-4,4-disubstituted cyclohexanones, which are readily available, could be transformed by a comparable series of steps to

(1) G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 4284 (1954).

(2) (a) A. Fürst and R. A. Plattner, Abstracts, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, p 409; (b) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953); (c) D. H. R. Barton and R. C. Cookson, *Quart. Rev.* (London), **10**, 67 (1956); (d) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).