g). A: mass spectrum m/e 494 (d_0, 20%), 495 (d_1, 39%), 496 (d_2, 33%), and 497 (d_3, 9%). B: mass spectrum m/e 494 (d_0, 19%), 495 (d_1, 40%), 496 (d_2, 32%), and 497 (d_3, 9%).

Michael Reaction of 2 with 1-*1-d*. 1-Iodofluorene. A 0.9-g portion of 1-aminofluorene[16] was diazotized in the usual way and the diazonium sulfate was decomposed in the presence of potassium iodide to yield 1-iodofluorene (0.39 g, 27%), mp 40–42°, mass spectrum m/e 292 (M^+) and 165.

Anal. Calcd for $C_{13}H_9I$: C, 53.45; H, 3.11. Found: C, 53.66; H, 2.94.

The title compound was oxidized with sodium bichromate in acetic acid to afford 1-iodofluorenone, mp 143.5–145° (lit.[17] mp 144–145°).

1-*1-d*. 1-*1-d* was obtained from 1-iodofluorene in an analogous manner from that of 1-*2,7-d_2*: mass spectrum m/e 166 (d_0, 26%), 167 (d_1, 63%), and 168 (d_2, 11%).

Michael Reaction of 2 with 1-*1-d*. A mixture of **2** and 1-*1-d* was treated as usual and afforded A-*1-d* (12% yield) and B-*1-d* (63% yield). A-*1-d*: mass spectrum m/e 494 (d_0, 35%), 495 (d_1, 57%), and 496 (d_2, 8%). B-*1-d*: mass spectrum m/e 494 (d_0, 36%), 495 (d_1, 60%), and 496 (d_2, 4%).

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Registry No.—**1**, 86-73-7; **2**, 746-47-4; **3**, 1530-12-7; A, 42759-04-6; B, 42759-03-5; hexahydrofluorene, 1559-97-3; 1,4-bis(2,2′-biphenylylene)-1,3-butadiene complex with 2,4,7-trinitrofluorenone, 54366-31-3; 9-methoxy-9,9′-bifluorenyl, 54366-32-4; 1-iodofluorene, 54366-33-5.

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Conformations of Vicinal Diesters

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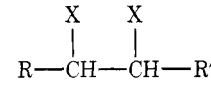
In diesters derived from 4-methyl-2,3-pentanediol, 1-phenyl-1,2-propanediol, and 3-methyl-1-phenyl-1,2-butanediol, the preference for gauche oxygen functions with respect to the ethanic backbone is nearly as large as for the diols themselves. Two reasons for the preference for gauche diester groups are possible: (a) dipolar attraction and (b) an intrinsic attraction related to electronegativity, but presently not well defined. Solvent effects and the effects of steric hindrance on conformation were studied, as well as ^{13}C chemical shifts and ^{13}C–H coupling constants. For erythro diesters, the data seem best interpreted in terms of an intrinsic attraction.

In their classic work on the application of NMR to problems in conformational analysis, Bothner-By and Naar-Colin observed rather unusual conformations for *meso*-2,3-diacetoxybutane (gauche ester functions).[1] Electrostatic attraction between the dipoles of the ester groups was considered to be a possible reason for this conformational preference. Later Schmid also reported unusual conformations for phenyl-substituted diesters.[2] However, substituted succinates show no well-defined preference for gauche carbonyl functions.[3,4]

Recent work by Abraham and Kemp showed that vicinal fluorine groups X preferred a gauche orientation despite sizable dipolar repulsion.[5] Phillips and Wray have correlated the tendency for X groups to occupy a gauche conformation with the total electronegativity of these groups.[6] However, Eliel and Kaloustian attributed the tendency for vicinal ether functions to be gauche to an attractive van der Waals interaction.[7] It is possible that electronegative X groups shrink the "size" of their respective lone pairs[8] so that the repulsions of the lone pairs is superseded by electron–nuclear attractions.[6,9] However, others have warned against too facile arguments involving the size of lone pairs.[8]

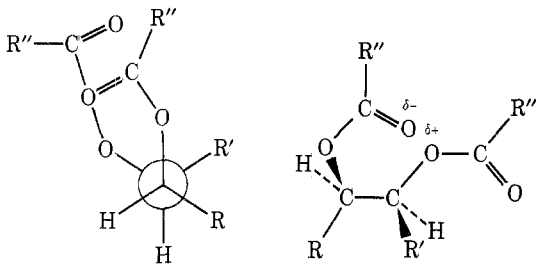


In a theoretical discussion of the reason for gauche X groups in 1,2-difluoroethane, Pople et al. considered the interaction of the two X groups to be repulsive, but this effect was counteracted by a hyperconjugative effect such that the electron withdrawal by an electronegative group X "partially empties the 2p orbital on carbon and facilitates the hyperconjugative electron delocalization by the neighboring CH_2 group".[10] On the other hand, Epiotis considers the interaction of two X groups to be attractive due to interaction of nonbonding pairs on the X groups forming antibonding and bonding combinations. The destabilizing ef-

fect of the antibonding combination is ameliorated because of charge transfer from this antibonding orbital into the unfilled antibonding orbital on the ethanic skeleton.[11] This treatment did not explain why other dihalides do not necessarily prefer a gauche conformation.[12] In theoretical calculations of the conformation of certain fluorine compounds, Abraham and coworkers suggested that no special explanations were necessary to account for the conformation.[13]

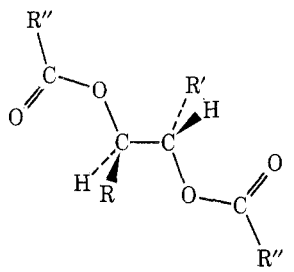
The chlorine groups of 2,2′-dichlorobiphenyls lie very close to one another in space, possibly indicative of an attractive interaction.[14] However, Zefirov and coworkers have suggested that interaction between second-row elements (e.g., sulfur–sulfur interactions) are more highly repulsive than interactions between first-row elements.[15,16]

Thus, in the molecules of interest in this study, vicinal diesters **1a–c**, two explanations might be applied to explain the preference of the ester functions for a gauche conformation: (1) dipolar attraction or (2) an intrinsic preference related to the electronegativity of the groups, whose nature is not completely elucidated as yet. The alkyl oxygens of the ester groups are rendered more electronegative than oxygens of analogous diols or diethers by resonance with the carbonyl, which places a partial positive charge on the alkyl oxygens. Molecular models suggest that conformation **1a**, which has maximum dipolar attraction, suffers from steric interactions between the R″ groups, if R″ is large. This steric interaction is alleviated in **1b**, but the dipolar attraction is not as large. Models suggest that **1c** would be the preferred conformation if only steric effects were important.



1a

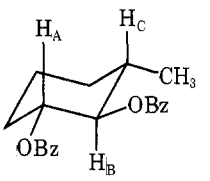
1b



1c

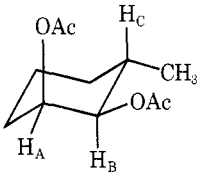
The purpose of this work is to attempt to distinguish between the two possible reasons for the presumed attraction between ester functions, and to establish the scope of the phenomenon. Solvent effects and the effect of size of R″, R′, and R will be discussed.

To attempt to establish the limiting NMR coupling constants for purely trans and purely gauche hydrogens, compounds **2–4** were investigated.[17] In **2**, near-conformational purity should be present; the coupling constant for the trans hydrogens A and B was ca. 10 Hz. This value seems rather small[18] perhaps owing to special factors present in the cyclohexane ring in this particular molecule (e.g., flattening to alleviate the sequential gauche interactions of the three equatorial groups),[1d] but this value will be taken as a rough approximation of the true value. In **3**, the relevant hydrogens are axial–equatorial in either of the major conformers; the averaged coupling contant for these gauche hydrogens is ca. 3 Hz.



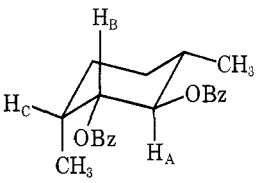
2

J_{AB} = 9.7 Hz
$J_{BC} \cong$ 9.8 Hz



3

J_{AB} = 2.9 Hz
J_{BC} = 10.2 Hz

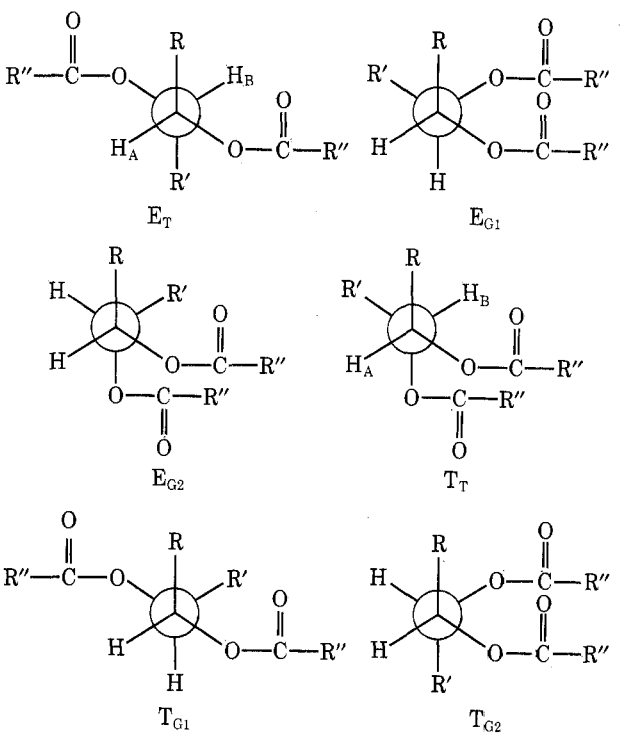


4

J_{AB} = 9.9 Hz
J_{BC} = 4.2 Hz

The NMR data for the acyclic compounds of interest are shown in Table I, in which older data on analogous diols are also included for comparison purposes.[19] These data may be interpreted in terms of the conformers shown in Scheme I (in which E_T signifies the conformer in the erythro set of isomers having trans hydrogens, etc.).

Scheme I



The conformation of the diesters (in CCl_4) is *roughly* similar to that of the diols, but the solvent effect is quite different. Intramolecular hydrogen bonding, of course, stabilizes the gauche hydroxyl groups of the diol. A sizable attractive interaction (but of somewhat smaller magnitude) must stabilize the gauche acetoxy functions (compare **5a** and **5b**, **6a** and **6b**).

The size of the ester function (specifically, R″) does not appear to have a large effect upon the conformation of the ethanic backbone.

Table I
100-MHz NMR Spectra of Vicinal Diesters

$$R-\underset{\displaystyle X}{\overset{\displaystyle |}{CH_A}}-\underset{\displaystyle X}{\overset{\displaystyle |}{CH_B}}-R'$$

Compd	R	R′	X	J_{AB} (J_{BC}), Hz[a] CCl_4	HOAc	CH_3CN	DMSO
Erythro 5a	CH_3	*i*-Pr	OH	3.3			6.0
5b			OAc	4.6 (7.2)		4.3 (7.5)	4.1 (7.4)
5c			OCOPh	5.5 (6.3)	4.3 (7.4)	4.0 (7.7)	4.0 (7.6)
Erythro 6a	CH_3	Ph	OH	4.0			5.3
6b			OAc	4.2	4.4	4.3	4.1
6c			OCOPh	4.1	4.2	4.3	4.3
6d			OCO-*i*-Pr	4.5			4.3
Erythro 7a	*i*-Pr	Ph	OH	5.8			7.5
7b			OAc	7.2			5.5
Threo 8a	CH_3	*i*-Pr	OH	5.9			5.3
8b			OAc	4.3 (7.2)	4.7 (7.0)	5.0 (6.7)	5.0 (6.6)
8d			OCO-*i*-Pr	4.8 (6.4)			~5.6
Threo 9a	CH_3	Ph	OH	7.5			6.4
9b			OAc	7.4	6.9	6.2	6.0
9c			OCOPh	7.7	7.5	6.5	6.6
9d			OCO-*i*-Pr	7.5		6.1	6.2
Threo 10a	*i*-Pr	Ph	OH	6.4			6.2
10b			OAc	6.0			5.8

[a] Where R′ is isopropyl, J_{BC} refers to the coupling constants of the CH(OCOR″)CH $(CH_3)_2$ fragment.

For the erythro isomers, the effect of increasing the size of R and/or R′ is to increase the population of conformer E_T (Scheme I). Conformer E_T minimizes the repulsive interaction of R and R′, but the mutual attraction of the ester functions is also eliminated. In the compounds studied, E_T is dominant only in the case of **7b**, where R = *i*-Pr and R′ = Ph, and then E_T is only slightly favored. Thus, it appears that a very large repulsion between R and R′ is necessary to overcome the attractive interaction of the ester groups.

For the threo isomers, no strong conformational preference is evident in any compound of this study. Conformer T_T is dominant by a small amount for **9**, but T_{G1} and/or T_{G2} are preferred for **8** and **10**.

The inability to distinguish between two conformers such as T_{G1} and T_{G2} has been one of the major problems in acyclic conformational analysis. This distinction can be made, in theory, with the aid of ^{13}C–H vicinal coupling constants.[3b,20,21] This technique has not been used frequently, but it is of great potential usefulness. Lemieux and coworkers have demonstrated that a Karplus type of dependence exists between dihedral angle and the ^{13}C–H coupling constant ($^3J_{CH}$). Limiting values of ca. 8 Hz were found for trans nuclei, and ca. 1 Hz for gauche nuclei in the compounds tested (certain carbohydrates).

In spectra of these natural abundance ^{13}C compounds, well-resolved splitting patterns could be obtained only for isolated methyl groups (Figure 1), or, in certain cases, for carbonyl groups. For **8b** and **8d**, the coupling constant between $^{13}CH_3$ and H_B was found to be 1.6 Hz (with a confidence level of ±0.4 Hz). For **9b** and **9d**, $^3J_{CH}$ was ca. 2 and 2.1 Hz, respectively.

For **8**, the fairly small J_{AB} values indicate a preference for a conformer having gauche hydrogens A and B. The $^3J_{CH}$ values suggest that methyl and H_B are predominantly gauche. Only conformer T_{G2} is consistent with both sets of data. For **9**, the "averaged" J_{AB} suggests that a mixture of conformers is present, whereas the $^3J_{CH}$ value suggests again a preference for conformers with gauche CH_3 and H_B groups. A mixture of T_T and T_{G2} accounts for these data. It seems reasonable that T_{G1} should not be highly populated in **8** and **9**, since R′ (phenyl or isopropyl) would be highly hindered and the ester functions would be trans.

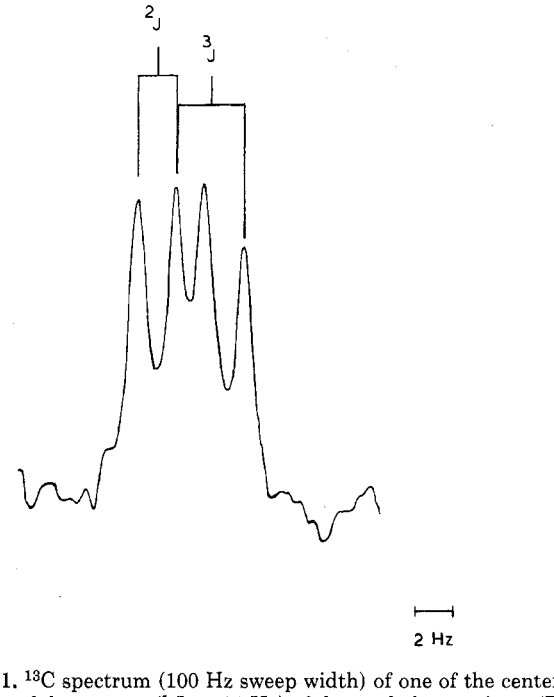


Figure 1. ^{13}C spectrum (100 Hz sweep width) of one of the center members of the quartet (^1J = 128 Hz) of the methyl group in **5c** (R = CH_3; R′ = *i*-Pr).

For the erythro compounds **5c**, **6b**, and **6d**, $^3J_{CH}$ was 3.8, 3.2, and 3.0 Hz, respectively. These values indicate that the conformer having trans $^{13}CH_3$ and H_B groups (E_{G1}) is more highly populated than its counterpart in the threo series.[22] In the alternative gauche H_A–H_B conformer, E_{G2}, phenyl or isopropyl is again highly hindered. However, $^3J_{CH}$ values have been determined in relatively few types of molecules

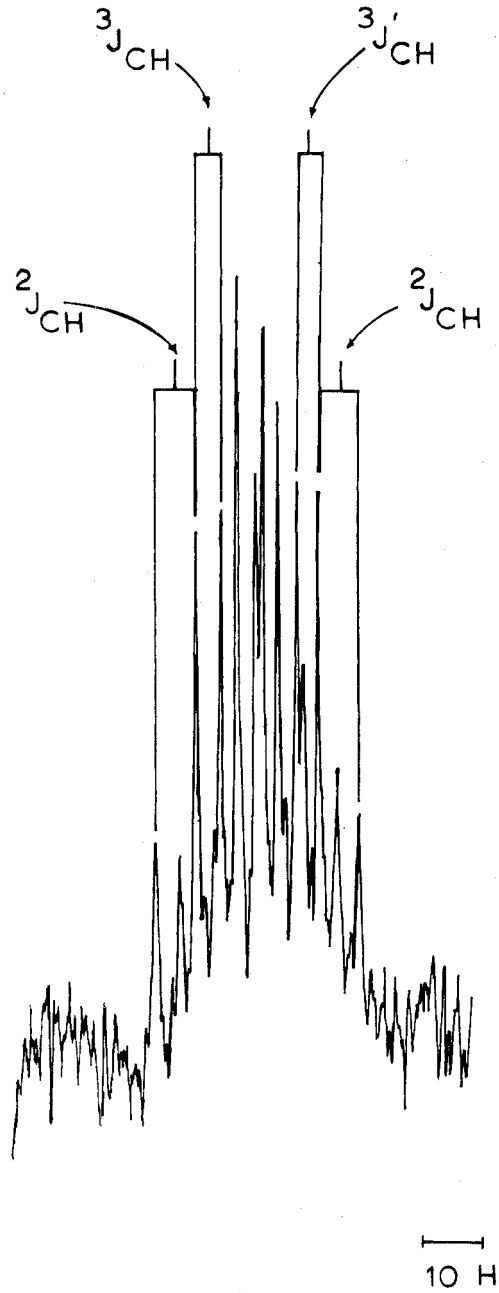


Figure 2. ^{13}C spectrum (500 Hz sweep width) of the carbonyl region for compound **8b** (R = CH_3; R′ = *i*-Pr). The pattern represents partially superposed double quartets, one for each OAc group. Each quartet is formed by coupling of the carbonyl carbon to the methyl group of the acetate ($^2J_{CH}$). Each doublet in the double quartet represents the coupling of carbonyl to H_A or H_B.

of known geometry, and the implication of $^3J_{CH}$ values must be regarded as rather tentative pending additional verification.

It was possible to determine well-resolved splitting patterns for the carbonyl carbons in two cases (Figure 2). For **8b**, $^3J_{CO-H}$ values of 3.6 and 4.2 Hz were observed for the two ester groups. Compound **6c** yielded similar coupling constants. The "averaged" value of $^3J_{CO-H}$, as observed in a methyl ester, has been reported as 4.5 Hz.[23] These data suggest that considerable rotational averaging is present for one ester group in **8b**.

As Table I shows, the effect of solvent upon conformation is rather complex. For **5** and **7**, a change from CCl_4 to a more polar solvent results in a *decrease* in J_{AB}, indicating that E_T diminishes and that E_{G1} and/or E_{G2} become more important. The increase in population of these conformers which have gauche X groups is similar to findings for dihalides[21] and dinitriles,[24,25] where repulsive, not attractive, interaction of the dipoles of the X groups is present. It seems likely that an attractive dipolar interaction between the ester groups (as in **1a**) would have been diminished by the interaction of the ester and solvent dipoles, leading to a lower preference for the E_G conformers.

The threo compounds populate a more "averaged" set of conformations on moving to the more polar solvents, which is not easily correlated with any simple solvent effect. For **8b**, no change is $^3J_{CH}$ was found (1.5 Hz) on moving from CCl_4 to DMSO.[7d,26] This suggests that the change in J_{AB} reflects a conversion from T_{G2} to T_T (both have gauche CH_3 and H_B groups).[27]

Carbonyl resonances have been shown to be sensitive to the changes in electron density associated with solvation.[28,29] It seemed likely that strong dipolar interactions, such as occur in **1a**, the face-to-face conformation, would also result in chemical shift changes. However, erythro and threo isomers having the same carbon skeleton show similar chemical shifts (Table II). Erythro **6b** and **7b**, which also occupy rather different sets of conformers, have similar carbonyl shifts. In **4**, the ester groups are confined near one another, but the carbonyl shifts are rather similar to those of **2** and **5c**. Thus, either the face-to-face conformation is not important, or, if it is, no large effect on ^{13}C chemical shifts results.[30] The change from an acetate (**8b**) to an isobutyrate (**8d**) results in a large chemical shift change for carbonyl, but no large effect upon the ^{13}C resonances of the hydrocarbon backbone is evident. This suggests that no large steric interaction between R″ and the carbon backbone is present.

In summary, for the erythro isomers the lack of an effect of R″ size, the solvent effect, and the rotational averaging of carbonyl are not consistent with a conformational preference dominated by dipolar attraction (as in **1a**), although forms such as **1b** are not necessarily excluded. One alternative proposal, that hyperconjugation leads to a preference for gauche X groups, is not supported by the sizable importance of T_T compared to T_{G2} (threo isomers). Hydrogens A and B are not properly situated for hyperconjugation in T_T as they are in T_{G2}.

Experimental Section

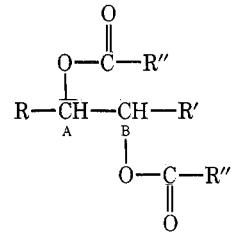
The general synthetic procedures involved the esterification of diols available from other studies,[19a] the use of the "dry" Prevost reaction, or the use of the "wet" Prevost reaction followed by esterification of the mixed half-esters.[31,32] Melting points are uncorrected.

***erythro*-4-Methyl-2,3-pentanediol Diacetate (5b). Procedure A.** Using the literature "wet" procedure,[32] a solution of 22.7 g (0.0875 mol) of iodine, 29.2 g (0.0175 mol) of silver acetate, and 7.0 g (0.0833 mol) of *cis*-4-methyl-2-pentene in 50 ml of acetic acid was converted to 9.7 g of the mixed half-esters (an oil).

Procedure B. According to literature procedures[32] the above half-esters were fully esterified: 0.58 g (3.6 mmol) of starting material was treated with 4 ml of acetic anhydride plus 0.2 g of sodium acetate, with a 20-hr reflux period. The crude product was distilled, bp 82–86° (7 mm) [lit.[33] bp 65–68° (2.5 mm)], giving 0.24 g (39%) of product: NMR (CCl_4) δ 0.88 [d, 3 $(CH_3)_2CH$], 0.95 [d, 3, $(CH_3)_2CH$], 1.1 [m, 1, $(CH_3)_2CH$], 1.90 (s, 3, OAc), 2.02 (s, 3, OAc), 4.7 [dd, 1, CHOAc), and 5.3 (dq, 1, CHOAc); ir (CCl_4) 2950, 2930, 1735, 1380, 1049, and 1025 cm^{-1}. The NMR spectrum also showed minor impurities that were not removed with repeated distillation.

***erythro*-4-Methyl-2,3-pentanediol Dibenzoate (5c). Procedure C.** Using the literature procedure for the "dry" Prevost,[32] a mixture of 5.09 g (0.22 mol) of silver benzoate [dried for 15 hr at 42° (ca. 1 mm)] and 2.82 g (0.011 mol) of *trans*-4-methyl-2-pentene in ca. 100 ml of dry benzene (distilled from calcium hydride) was refluxed for 20 hr under nitrogen with mechanical stirring. The literature work-up was used except that the product was not distilled owing to discoloration of the product. Chromatography on silica gel (Baker) using increasing amounts of ether in pentane as

Table II
^{13}C Chemical Shifts



Compd	R	R'	R''	^{13}C chemical shift, ppm[b]						
				C=O	R''	C_A	C_B	CH_3	$(CH_3)_2CH$	
5c	CH_3	*i*-Pr	Ph	165.8		70.3	78.9	15.0	19.2	29.3
				165.5					18.0	
6b	CH_3	Ph	CH_3	169.9	21.0	71.6	75.6	14.6		
				169.5	21.0					
7b	*i*-Pr	Ph	CH_3	170.2	21.0	78.5	75.2		19.5	28.3
				169.6	20.8				16.6	
8b	CH_3	*i*-Pr	CH_3	170.5	21.4	69.4	79.0	16.6	19.0	28.7
				170.1	21.3					
8d	CH_3	*i*-Pr	*i*-Pr	176.2	*a*	69.2	78.3	16.6	19.1	28.7
				176.0	*a*				17.1	
9b	CH_3	Ph	CH_3	170.0	21.0	71.4	76.3	16.5		
				169.6	20.8					
10b	*i*-Pr	Ph	CH_3	170.0	21.1	77.7	74.3		19.5	28.7
				169.5	20.6				17.2	
2	Cyclic		Ph	166.2		75.3	78.8	17.9		
				165.8						
4	Cyclic		Ph	166.2		76.9	75.0	18.0		
				165.6				12.8		

[a] Complex nonequivalent methyl signals present. [b] Vs. Me_4Si as 0 ppm.

eluents followed by rotary evaporation gave product that appeared pure by all spectral methods and so distillation was not attempted [lit.[34] bp 153° (0.1 mm)]: yield 2.06 g (63%); NMR (CCl_4) δ 0.99 [d, 3, $(CH_3)_2CH$], 1.09 [d, 3, $(CH_3)_2CH$], 1.39 (d, 3, CH_3), 2.0 [m, 1, $(CH_3)_2CH$], 5.36 (m, 2, CH(OBz), and 7.05–8.15 (m, 10, Ar); ir (CCl_4) 3023, 3006, 2915, 1730, 1595, 1480, 1350, 1310, 1145, and 1050 cm^{-1}.

***erythro*-1-Phenyl-1,2-propanediol Diacetate (6b).** The ester was prepared by procedure B from 0.50 g (3.3 mol) of 1-phenyl-1,2-propanediol, 0.2 g of sodium acetate, and 4 ml of acetic anhydride. The crude diester was chromatographed on 185 g of silica gel using ether–pentane mixtures. The product appeared pure, and distillation was not attempted [lit.[35] bp 109° (0.4 mm)]: NMR (CCl_4) δ 1.14 (d, 3, CH_3), 1.89 (s, 3, OAc), 2.03 (s, 3, OAc), 5.13 (dq, 1, CHOAc), 5.91 (d, 1, CHPh), and 7.3 (s, 5, Ph).

***erythro*-1-Phenyl-1,2-propanediol Dibenzoate (6c).** This material was prepared by procedure C in 38% yield. Several recrystallizations from methanol gave 4.6 g (38%) of product: mp 95–96° (lit.[36] mp 96–97°); NMR (CCl_4) δ 1.38 (d, 3, CH_3), 5.57 (dq, 1, $CHCH_3$), 6.29 (d, 1, CHPh), 7.27 (s, 5, Ph), and 7.1–8.2 (m, 5, Ar); ir (CCl_4) 3110, 3085, 3050, 3007, 1760, 1748, 1604, 1453, 1160, 1120, 1100, 1075, 1060, and 760 cm^{-1}.

***erythro*-1-Phenyl-1,2-propanediol Diisobutyrate (6d). Procedure D.** A mixture of 0.52 g (0.034 mol) of the parent diol, 2 ml of isobutyryl chloride, and 10 ml of pyridine was refluxed for 24 hr. The remaining solids were washed with ethyl acetate, and the combined organic filtrates were extracted with two 15-ml portions of 10% HCl and with dilute sodium bicarbonate solution and dried ($MgSO_4$). Rotary evaporation of the solvent gave an oil which was chromatographed on ca. 150 g of silica gel using ether–hexane eluents. Certain intermediate fractions showed high purity, and distillation again was not attempted. The pure fractions weighed 0.68 g (68% yield): NMR (CCl_4) δ 0.98–1.28 (complex methyl doublets), 2.48 [m, 2, $(CH_3)_2$ CH], 5.26 (dq, 1, $CHCH_3$), 5.71 (d, 1, CHPh), and 7.29 (s, 5, Ph); mass spectrum (20 eV) *m/e* (rel intensity) 248 (54), 204 (94), 178 (16), 177 (100), 176 (7), 134 (21), 117 (8), and 71 (6); *m/e* 248 represents M^+ − isobutyric acid.

***erythro*-1-Phenyl-3-methyl-1,2-butanediol Diacetate (7b).** This material was prepared by a slight variant of procedure D in 56% yield: NMR δ 0.91 [broad d, 6, $(CH_3)_2CH$], 1.96 (s, 3, OAc), 2.00 (s, 3, OAc), 5.11 (dd, 1, CHOAc), 5.82 (d, 1, CHOAc), and 7.32 (s, 5, Ph); mass spectrum (20 eV) *m/e* (rel intensity) 212 (1), 205 (5), 204 (26), 192 (9), 162 (8), 150 (12), 149 (100), 115 (10), 107 (56), and 42 (35); *m/e* 149 and 115 represent PhCH(OAc) and *i*-C_3H_7CHOAc, respectively.

***threo*-4-Methyl-2,3-pentanediol Diacetate (8b).** This material was prepared by procedures A (35% yield) and B (39% yield), bp 89–92° (8 mm) [lit.[33] bp 81–82° (25 mm)]. Later work showed that chromatography on silica gel and film drying (no distillation) was preferable: NMR (CCl_4) δ 0.82 [d, 3, $(CH_3)CH$], 0.93 [d, 3, $(CH_3)_2CH$], 1.10 (d, 3, CH_3CHOAc), 1.0–1.4 [m, 1, $(CH_3)_2CH$], 1.95 (s, 3, OAc), 2.03 (s, 3, OAc), 4.65 (dd, 1, CHOAc), and 5.02 (dq, 1, CHOAc).

***threo*-4-Methyl-2,3-pentanediol Dibenzoate (8c).** This material was prepared by procedure D (17% yield). The oil was chromatographed on 200 g of silica gel with pentane–ether eluents, yielding 0.237 g (17%) of pure product [lit.[34] bp 143° (0.06 mm)]: NMR (CCl_4) δ 0.96 [d, 6, $(CH_3)_2CH$], 1.28 (d, 3, CH_3), 2.06 [m, 1, $(CH_3)_2CH$], 5.1 (dd, 1, CHOBz), 5.4 (dq, 1, $CHCH_3$), and 7.2–8.2 (m, 10, Bz).

***threo*-4-Methyl-2,3-pentanediol Diisobutyrate (8d).** This product was prepared by procedure D (56% yield). The resulting oil was purified by chromatography on silica gel: NMR (CCl_4) δ 0.9–2.0 (complex methyl doublets), 4.75 [dd, 1, $CHCH(CH_3)_2$], and 5.05 (dq, 1, CH_3CH); mass spectrum (70 eV) *m/e* (rel intensity) 215 (9), 171 (21), 143 (100), 142 (95), 115 (52), 100 (26), 83 (50), 72 (36), 71 (68), and 43 (86). The *m/e* 143 and 115 peaks represent cleavage of the ion at the bond joining the isobutyroxy groups.

***threo*-1-Phenyl-1,2-propanediol Diacetate (9b).** This material was prepared by procedure A (85% yield) and B (62% yield): bp 106–112° (1 mm) [lit.[35] bp 112–116° (0.7–0.9 mm)]; NMR (CCl_4) δ 1.04 (d, 3, CH_3), 1.94 (s, 3, OAc), 2.01 (s, 3, OAc), 5.20 (dq, 1, $CHCH_3$), 5.71 (d, 1, CHPh), and 7.30 (s, 5, Ph); ir (CCl_4) 3010, 1734, 1370, 1225, and 709 cm^{-1}.

***threo*-1-Phenyl-1,2-propanediol Dibenzoate (9c).** This material was prepared by procedure C (76% yield): mp 95–96° (lit.[36] mp

96–97°); NMR (CCl_4) δ 1.38 (d, 3, CH_3), 5.57 (dq, 1, $CHCH_3$), 6.29 (d, 1, CHPh), 7.27 (s, 5, Ph), and 7.1–8.2 (m, 10, Ar).

***threo*-1-Phenyl-1,2-propanediol Diisobutyrate (9d).** The parent diol (0.52 g, 2.4 mmol) was converted to the diester by procedure D, yielding 0.73 (73%) of product: NMR (CCl_4) δ 1.0–1.3 (complex series of methyl doublets), 2.5 [m, 2, $(CH_3)_2CH$], 5.25 (m, 1, $CHCH_3$), 5.71 (d, 1, CHPh), 7.31 (s, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 248 (7), 204 (12), 177 (46), 135 (12), 71 (100), 43 (20); *m/e* 248 represents M^+ − isobutyric acid; *m/e* 177 represents $PhCHOC(=O)C_3H_7$.

***threo*-1-Phenyl-3-methyl-1,2-butanediol Diacetate (10b).** Using procedure A, 2.0 g (0.014 mol) of *trans*-1-phenyl-3-methyl-1-butene was converted to 2.0 g (66%) of the mixed half-esters. Using procedure B, 1.0 g (4.5 mol) of the half-esters were acetylated; chromatography of the product on silica gel afforded considerable quantities of a material having only one acetoxy NMR peak, which blended with the desired product. Only 0.3 g (25%) of the desired diester could be isolated: NMR (CCl_4) δ 0.89 [d, 3, $(CH_3)_2CH$], 0.99 [d, 3, $(CH_3)_2CH$], 1.83 (s, 3, OAc), 2.00 (s, 3, OAc), 5.07 (dd, 1, CHOAc), 583, (d, 1, CHPh), and 7.27 (s, 5, Ph); mass spectrum (20 eV) *m/e* (rel intensity) 204 (30), 149 (100), 115 (10), 107 (63), 68 (21), 63 (19), and 43 (45).

3-Methyl-1,2-cyclohexanediol Dibenzoate (2). Using procedure D, the crude parent diol (mixture of isomers (0.3 g, 2.3 mmol) was esterified (20% yield of the desired isomeric product) and purified by chromatography on silica gel: NMR ($CDCl_3$, 100 MHz) δ 0.88 (d, 3, CH_3), 1.1–1.8 (broad m, 6, ring hydrogens), 2.16 (broad m, 1, ring hydrogen), 2.16 (broad m, 2, ring hydrogen), 5.01 (broad m, 2, CHOBz), 7.1–8.1 (m, 10, Ar); mass spectrum (20 eV) *m/e* (rel intensity) 321 (9), 230 (26), 227 (2), 226 (36), 131 (4), 109 (11), 108 (42), 106 (9), 105 (100), and 93 (11).

3-Methyl-1,2-cyclohexanediol Diacetate (3). Using procedure A, 10.0 g (0.10 mol) of 3-methylcyclohexene, 27.7 g (0.11 mol) of iodine, and 26.5 g (0.22 mol) of silver acetate were converted to 21.5 g of the mixed half-esters. Using procedure B, 20.5 g of the mixed half-esters was acetylated, giving 13.9 g of crude diester **3**. Distillation at 9 mm gave the following fractions: boiling at 109–113°, 3.3 g, and 113–119°, 3.93 g. Both fractions were somewhat impure, showing an additional acetoxy peak in the NMR. Chromatography of a portion of the second fraction on silica gel gave essentially pure **3**, which, however, was slightly contaminated with another isomer of the same general structure: NMR ($CDCl_3$, 100 MHz) δ 0.86 (d, 3, CH_3), 1.4–2.3 (broad m's, ring hydrogens), 1.94 (s, 3, OAc), 2.01 (s, 3, OAc), 4.47 (dd, 1, J = 2.9, 10.3 Hz, CHOAc), and 5.19 (m, 1, CHOAc); mass spectrum (20 eV) *m/e* (rel intensity) 155 (6), 154 (6), 113 (21), 112 (100), 111 (42), 97 (46), 95 (85), 94 (99), 79 (80), and 43 (72); *m/e* 155 represents M^+ − acetic acid.

3,6-Dimethyl-1,2-cyclohexanediol Dibenzoate (4). Using procedure C, 1.96 g (0.0169 mol) of 3,6-dimethylcyclohexene, 4.31 g (0.0169 mol) of iodine, and 7.96 g (0.0339 mol) of silver benzoate were allowed to react, and the crude product was chromatographed on silica gel. The early fractions contained considerable quantities of a material lacking one benzoate. A material isomeric with **4** was obtained in fraction 5, but it could not be adequately purified. The desired product was obtained in fractions 8–12 totaling 0.52 g (9%): NMR ($CDCl_3$, 100 MHz) δ 0.90 (d, 3, CH_3), 0.96 (d, 3, CH_3), 1.31–1.87 (m, 5, ring hydrogens), 2.3–2.6 (m, 1, ring hydrogen), 5.13 (dd, 1, CHOBz), 5.25 (apparent t, 1, CHOBz), 7.06–7.42 (m, 6, *m*-, *p*-Bz), 7.77–8.05 (m, 4, *o*-Bz); mass spectrum (20 eV) *m/e* (rel intensity) 216 (1), 123 (33), 122 (100), 106 (12), 105 (87), 77 (28), and 43 (3). Peaks *m/e* 122 and 105 represent C_6H_5COOH and $C_6H_5CO^+$, respectively.

NMR Spectra. These spectra were taken on a Varian XL-100 instrument or, in a few cases, on a Varian A-60D. For **5–10** the spectra were (CCl_4 solution) simulated using the LAOCOON III program adapted to provide a computer-generated plot of the input parameters. The parameters were adjusted until the computer plot was superimposible upon the spectrometer plot. Coupling constants were determined from the average of several traces of expanded spectra. The concentration of the solutions for the proton spectra of **5–10** was 2.5%, except for **7b, 9b,** and **10b** in DMSO (5%).

The spectra listed in Table I were taken at 100 MHz, whereas the spectra listed in the Experimental Section were taken at 60 MHz, except as noted, at rather variable concentrations. The solvent for **2–4** was $CDCl_3$ (ca. 10% w/v). The spectra for **2–4** were not simulated; however, the coupling constants quoted for **3** were essentially the same at 60 and at 100 MHz as taken directly from the spectra. For **4**, the validity of the coupling constants was verified by selectively decoupling protons A and B from other intefering protons. Although the pattern changed in the decoupling experiments, the line separation resulting rom the A–B coupling was essentially invariant. For **2**, both spin decoupling and the addition of $Eu(fod)_3$ were necessary in order to attain a clear spectrum. Although several accounts of the change in conformation upon the addition of $Eu(fod)_3$ have been published, variable amounts of $Eu(fod)_3$ gave little or no change in the basic line separations quoted.

The ^{13}C spectra were determined in 12-mm tubes using as high a concentration of substrate as possible (usually 10% w/v in $CDCl_3$, if sufficient substrate was available). In a typical run, i.e., for **2**, a 5000-Hz spectral width was used, with a 0.4-sec acquisition time, and a pulse delay of 0.1 sec; 5.2 K of transients were collected using a pulse width of 30 μsec. The maximum resolution, as calculated by the computer, was 0.0992 ppm. The chemical shifts were determined from the computer listing of the peaks, with respect to the middle line of $CDCl_3$, which was taken as 76.9 ppm from TMS, the ultimate standard.

In order to determine the ^{13}C–H coupling constants, a narrower "window" (either 500 or 1000 Hz) was used in order to improve resolution. Either the gated mode of operation was used,[37] or, in some cases, the decoupler was not used. The coupling constants were determined from the average of several measurements (somewhat more variability was noted for these line separations compared to H–H couplings, perhaps owing to digitization). In practice, only measurement of coupling constants to carbons of isolated methyl groups was possible in the machine time that was available; the signals for other carbons tended to be unresolved multiplets.

In the expanded spectra such as in Figure 1, it was difficult to tell ^2J from ^3J. The constant line separation observed in all compounds, ca. 2.1 Hz, was taken as ^2J. The ^{13}C–H couplings were simulated using the LAOCOON III program. The spectra were shown to be subject to first-order interpretation in most cases, although in other cases (**5** and **8**) small adjustments were necessary to make the simulated spectrum fit the original.

Registry No.—**2,** 54382-87-5; **3,** 42282-50-8; **4,** 54354-06-2; **5a,** 6702-10-9; **5b,** 54354-07-3; **5c,** 4265-29-6; **6a,** 1075-04-3; **6b,** 21145-69-7; **6c,** 21759-65-9; **6d,** 54354-08-4; **7a,** 19776-13-7; **7b,** 54354-09-5; **8a,** 6464-40-0; **8b,** 54354-10-8; **8c,** 4306-97-2; **8d,** 54354-11-9; **9a,** 1075-05-4; **9b,** 21145-70-0; **9c,** 21759-66-0; **9d,** 54354-12-0; **10a,** 19776-14-8; **10b,** 54354-13-1; isobutyryl chloride, 79-30-1; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; 3-methyl-1,2-cyclohexanediol, 23477-91-0.

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Conformational Analysis. Effect of a Vicinal Hydroxyl Group on the Methylation Rates of Cyclohexyldimethylamines and *trans*-Decalyldimethylamines

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The rates of methylation of the four 3-dimethylamino-*trans*-2-decahydronaphthols, of the *cis*- and *trans*-2-dimethylaminocyclohexanols, as well as those of the corresponding "parent" amines have been measured as a function of temperature. The rate of the *cis*-3-dimethylamino-*trans*-decahydronaphthol **2** is found to be unusually high for a compound with an axial dimethylamino group and confirms the flattened chair conformation assigned to this compound. The difference in reactivity between axial and equatorial dimethylamino groups seems to be of steric origin (a much more restricted transition state in the former case). An unusual feature of the reaction is that in cases involving an equatorial dimethylamino group the rate constant of the diequatorial isomer is significantly much lower than that of the isomer with an axial hydroxyl group.

Although the reaction of alkyl halides with tertiary amines (Menschutkin reaction) has been extensively studied,[3] there is relatively little information regarding the rates of alkylation of simple conformationally stable exocyclic amines.[4-6] In this work we report the rates of methylation in acetonitrile of the four 3-dimethylamino-*trans*-2-decahydronaphthols (**1**, **2**, **3** and **4**), of the *trans*- and *cis*-dimethylaminocyclohexanols (**5** and **6**), and of the corresponding parent amines (**7**, **8**, and **9**).

Results and Discussion

The results of the methylation of the four 3-dimethylamino-*trans*-2-decahydronaphthols (**1–4**), of the *trans*- and *cis*-dimethylaminocyclohexanols (**5** and **6**), of the *trans*- and *cis*-2-decalyldimethylamines (**7** and **8**), and of the cyclohexyldimethylamine are summarized in Table I. The kinetic measurements have been effected in acetonitrile so as to compare them with Allinger's results on *tert*-butylcyclohexylamines. Acetonitrile being in fact a good proton acceptor, it had to be checked that no competition was taking place between the intramolecular H bond and H bond with acetonitrile; to settle this point we have observed the NMR spectra in this solvent and we do not find any variation in half-width band height for the proton α to the substituent. Furthermore, for the compound **2**, deformed by a strong H bond, one finds a value of 22 Hz for the $W_{1/2}$ of the proton α to OH, this value being the same in $CDCl_3$.

The rates constants were evaluated graphically; these values are the average of at least three independant determinations.

The values of $\Delta H^{\ddagger}$ were obtained from the gradient of plots of log k/T against the reciprocal of the absolute temperature; the values of $\Delta S^{\ddagger}$ were obtained from the Eyring equation, i.e., from the gradient of T log k/T against T. The precision of the value of k_2 is of the order of 1%. The error of the $\Delta S^{\ddagger}$ value is of the order of 1 eu.

First, it may be noted that the compounds in which the dimethylamino group occupies an axial position react more slowly than those in which this group occupies an equatorial position. This is what one would expect, inasmuch as it is experimentally known that axial groups undergo reactions at reduced rates when compared to equatorial groups, in