Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.93; H, 11.09.

This reaction was repeated in pure THF at room temperature with 2.29 g (0.094 g-atom) of magnesium in 175 ml of THF, 8.80 g (0.041 mol) of 1,4-dibromobutane in 200 ml of THF, and 3.81 g (0.023 mol) of **4a** in 175 ml of THF. The products isolated consisted of 2-methylcycloheptanone (10%) and 6-methyl-5-undecanone (90%) which were compared with authentic samples. Only a trace (0.2%) of the unsaturated aldehyde **34** was detected.

Registry No.—**7**, 39575-86-5; **19**, 25368-59-6; **20**, 39575-88-7; **23**, 39575-89-8; **24**, 39575-90-1; **25**, 36871-42-8; **26**, 39575-92-3; **27**, 39575-93-4; **33**, 932-56-9; **34**, 17206-63-2; 2-benzyl-4,4,6-trimethyloxazine, 26939-22-0; paraformaldehyde, 30525-89-4.

Acknowledgment.—The authors are grateful to the National Science Foundation (GP 22541), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health for financial support of this work. Generous supplies of organolithium reagents from the Lithium Corporation of America are also gratefully acknowledged.

Correlation of Configuration and ^{19}F Chemical Shifts of α-Methoxy-α-trifluoromethylphenylacetate Derivatives[1]

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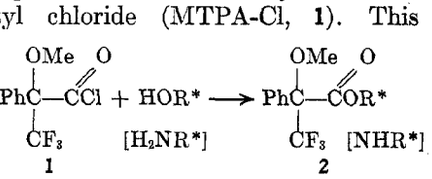
An empirically derived correlation of configuration of diastereomeric α-methoxy-α-trifluoromethylphenylacetic (MTPA) esters and amides with the ^{19}F chemical shifts has been developed. The data have been rationalized in terms of a configuration-correlation model **5**. The inherently large ^{19}F chemical shifts ($CDCl_3$ solvent, external trifluoroacetic acid) and their location in an otherwise uncongested region of the nmr spectrum makes this correlation of considerable value in connection with stereochemical studies involving chiral secondary alcohols and primary amines. Of the 25 examples studied, 19 MTPA esters and 6 MTPA amides, 18 clearly group themselves in a general pattern which is discussed in terms of the configuration-correlation model. Three MTPA esters showed no significant chemical shift nonequivalence for the ^{19}F α-CF_3 signals between *R,R–S,S vs. R,S–S,R* diastereomers. Of the four cases which might be considered exceptions to this nmr configurational correlation model, namely isobutyl-*tert*-butylcarbinol, *n*-butyl-*tert*-butylcarbinol, trifluoromethyl-*tert*-butylcarbinol, and borneol, the first three can be rationalized while only borneol stands as a clear exception to the model. All of the 6 MTPA diastereomeric amides studied conform to the same model.

The nonequivalence of various diastereomeric esters and amides has been utilized for the quantitative determination of enantiomeric composition of chiral alcohols and amines.[3] These studies recently have been extended to include correlations of configurations with proton nmr chemical shift differences of these diastereomers.[4] We now report on an empirically derived correlation of configuration and ^{19}F nmr chemical shift differences for esters and amides of α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) which are readily prepared from α-methoxy-α-trifluoromethylphenylacetyl chloride (MTPA-Cl, **1**). This derivative was chosen because of its availability in optically active forms,[3c,5] stability to racemization, and proven utility in earlier proton nmr studies.[4]



1 2

This method has the inherent advantage that the ^{19}F nmr chemical shift differences for the α-CF_3 group of such diastereomeric derivatives (**2**) are generally greater than those of the corresponding proton signals in the same compounds. With the usual substrates the ^{19}F signals are found in a completely unobstructed region of the spectrum. If there are other fluorine substituents on the carbinyl moiety of the MTPA esters or amides, their signals are generally discernible by spin–spin coupling patterns.

The ^{19}F chemical shifts for the diastereomers in this study are listed in Table I. They are recorded in parts per million downfield relative to external trifluoroacetic acid (TFA) in deuteriochloroform solvent. From these data are obtained the diastereomer chemical shift differences ($\delta_X - \delta_Y$). These values are also compared to those reported previously[3c] using internal TFA as a reference standard (Table I, last three columns). In our previous studies we had noted that internal TFA, as well as solvent, had a pronounced effect on the position of the α-CF_3 resonances and on the chemical shift differences of the α-CF_3 signals of diastereomeric MTPA esters. We further observed that in some cases there was no diastereomer chemical shift difference for these α-CF_3 until TFA was added. These initial observations had discouraged us from seriously considering a correlation scheme based upon the nonequivalence of these α-CF_3 resonances. We now find that, in spite of the fact that some MTPA diastereomers give coincident α-CF_3 signals in the absence of TFA (3 out of 25 examples in Table I), very significant nonequivalences are observed in most cases. In the present study all values were obtained using external TFA.

(1) We acknowledge with gratitude support of these studies by the National Science Foundation, Grant GP 27448.

(2) Taken in part from the Ph.D. Thesis of James A. Dale, Stanford University, 1970.

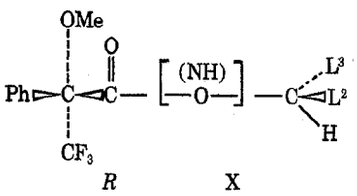
(3) (a) M. Raban and K. Mislow, *Tetrahedron Lett.*, 4249 (1966); (b) *Top. Stereochem.*, **2**, 199 (1967); (c) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969); (d) J. A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, **90**, 3732 (1968); (e) G. Helmchen, R. Ott, and K. Sauber, *Tetrahedron Lett.*, 3873 (1972).

(4) J. A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, **95**, 512 (1973), and references cited therein.

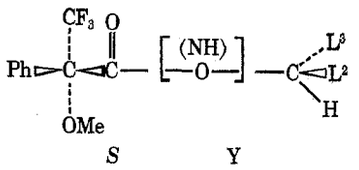
(5) Resolved MTPA[5d] is available from Aldrich Chemical Co., Inc., Milwaukee, Wis., Norse Chemicals, Santa Barbara, Calif., and Fluka AG, Buchs, Switzerland.

TABLE I

^{19}F NMR CHEMICAL SHIFT DIFFERENCES FOR DIASTEREOMERIC MTPA DERIVATIVES[a]



R X



S Y

Registry no. X	Registry no. Y	Carbinol moiety L²	Carbinol moiety L³	Configuration[b]	Nmr chemical shift of α-CF₃, downfield from TFA[c] External TFA[a] −δX, ppm	External TFA[a] −δY, ppm	External TFA[a] (−δX) − (−δY), ppm	Internal TFA[a] −δX, ppm	Internal TFA[a] −δY, ppm	Internal TFA[a] (−δX) − (−δY), ppm
20445-05-0	39532-60-0	Me	Et	R[d]	7.25	7.25	0.0	5.73	5.65	0.08
20445-07-2	39532-61-1	Me	*i*-Pr	R[d]	6.57	6.39	0.18	6.17	6.00	0.17
20445-09-4	39532-62-2	Me	*n*-Hex	R[d]	7.31	7.26	0.05	6.12	5.80	0.32
20445-13-0	39532-63-3	Me	CF_3	R[e]	7.00	6.63	0.37	4.48	4.20	0.28
20445-11-8	39532-64-4	Me	*t*-Bu	R[f]	6.79	6.57	0.22	6.39	6.17	0.22
39532-26-8	39532-65-5	Me	CO_2Et	R[g]	7.09	6.64	0.45			
39532-27-9	39532-66-6	Me	CH_2NMe_2	R[h]	7.85	7.71	0.14			
39532-28-0	39532-67-7	*t*-Bu	CF_3	R[e]	7.67	6.94	0.73	6.38	6.38	0.0
39532-29-1	39532-68-8	*t*-Bu	*i*-Bu	S[f]	8.11	7.71	0.40			
39532-30-4	39532-69-9	Me	Ph	R[i]	7.97	7.77	0.20	5.81	5.30	0.51
39532-31-5	39532-70-2	*n*-Pr	Ph	R[i]	7.92	7.65	0.27			
39532-33-7	39532-71-3	*i*-Pr	Ph	R[i]	8.15	7.80	0.35			
20445-20-9	39532-47-3	*t*-Bu	Ph	R[i]	8.43	8.00	0.43	7.12	6.62	0.50
20445-16-3	39532-48-4	CF_3	Ph	S[e]	6.95	6.95	0.0	5.86	5.32	0.54
39532-36-0	39532-49-5	*t*-Bu	*n*-Bu	S[f]	7.96	7.71	0.25			
39532-37-1	39532-50-8	Ph	Trityl	R[j]	7.27	7.13	0.14			
39532-44-0	39532-51-9		*d*-Bornyl	S[k]	7.37	7.27	0.10			
39532-38-2	39532-52-0		*l*-Menthyl	R[l]	7.46	7.34	0.12			
39532-45-1	39532-53-1		Cholesteryl	S	7.17	7.17	0.0			
		Amine moiety								
39532-46-2	39532-54-2	Me	Et	R[d]	10.51	10.41	0.10			
39532-39-3	39532-55-3	Me	*n*-Hex	R[m]	9.90	9.81	0.09			
20445-26-5	39532-56-4	Me	Ph	R[m]	8.02	7.77	0.25	7.55	7.30	0.25
20445-24-3	39532-57-5	Me	CH_2Ph	R[d]	10.66	10.35	0.31	7.39	6.89	0.50
39532-42-8	39532-58-6	Me	α-Naph	R[n]	10.87	10.58	0.29	7.85	7.39	0.46
39532-43-9	39532-59-7		*l*-Menthyl	R[l]	9.94	9.84	0.10			

[a] Data determined at 94.1 MHz on a Varian XL-100 spectrometer using deuteriochloroform solvent, with trifluoroacetic acid (TFA) external standard; internal TFA, ref 3c. [b] Configurations as per formulas X and Y in the heading. The actual data may have been determined on the opposite isomer but corrected for the configuration shown. [c] The convention used for reporting chemical shifts is such that signals upfield from TFA have positive values and signals downfield from TFA have negative values. All chemical shifts reported here are downfield from TFA. [d] J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 177 (1954); J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959). [e] H. Peters, D. M. Feigl, and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968). [f] W. M. Foley, F. J. Welch, E. M. LaCombe, and H. S. Mosher, *J. Amer. Chem. Soc.*, **81**, 2779 (1959). [g] J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 187 (1954). [h] A. H. Beckett, N. J. Harper, and J. W. Cletherow, *J. Pharm. Pharmacol.*, **15**, 8577g (1963). [i] R. MacLeod, F. J. Welch, and H. S. Mosher, *J. Amer. Chem. Soc.*, **82**, 876 (1960). [j] V. Prelog, E. Philbin, E. Watanabe, and M. Wilhelm, *Helv. Chim. Acta*, **39**, 1086 (1956). [k] Configuration at carbinyl center; the 2 position is designated L^2 and the 6 position L^3. This example is complicated by multiple chiral centers. [l] (−)-Menthyl configuration at carbinyl carbon, in which the α-isopropyl substituent is designated L^3 and the α-methylene as L^2. For configuration see J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. 1, 2nd ed, Cambridge University Press, London, 1947, p 245. [m] J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959). [n] M. G. B. Drew, *Acta Crystallogr.*, **B25**, 1320 (1971).

Table I has been so organized that the configurations of the carbinyl moiety in X and Y are the same, while those of the MTPA moiety are *R* in X and *S* in Y. The enantiomers of X and Y will of course have identical nmr spectra. Thus Table I accommodates the data for the configurations shown as well as those for the enantiomers of X and Y. These data will be first considered from a strictly empirical viewpoint followed by an attempt to rationalize them in terms of a conformationally based stereochemical correlation model.

The chemical shift data in Table I are arranged so that the α-CF_3 group of diastereomer X has its resonance to lower field than that of Y. Once this is done, the designation of the groups on the carbinyl carbon as L^2 *vs.* L^3 is not arbitrary since each example in Table I is of known configuration. The data for any new MTPA ester or amide can be fitted into Table I in like manner; however, if the configuration of such a new example is unknown, then there is a choice which must be made for the designation of the substituents attached to the carbinyl carbon as either L^2 or L^3. This designation of L^2 and L^3 serves to establish the assigned configuration of X and Y. Without additional information such a designation would be arbitrary. An inspection of columns 3 and 4 of Table I shows that in all but four somewhat special cases the L^2 group is "smaller" than the L^3 group. The decision as to which of two groups is sterically smaller is very clear in cases such as methyl *vs.* *tert*-butyl and methyl

vs. phenyl, but it is not so obvious in cases such as *tert*-butyl *vs.* phenyl, trifluoromethyl, isobutyl, or even *n*-butyl. This problem has been discussed in general.[6] Nevertheless, *if it is possible to decisively designate one group attached to the carbinyl carbon as sterically smaller than the other group*, then by specifying the "smaller group" L^2 and the "larger group" L^3 the new example will fit the general pattern of the data in Table I. Thus the configuration of such a new compound can be determined by this empirical correlation. The specification of the carbinyl moiety as *R* or *S* follows from the application of the Cahn–Ingold–Prelog configurational nomenclature rules. It is important to note that steric bulk considerations alone may be invalid for electronegative groups such as CF_3 and for groups containing other heteroatoms.

The six MTPA amides of primary amines which are chiral at the carbinyl carbon, in analogy with the secondary carbinols, show completely comparable nmr nonequivalences for the α-CF_3 resonances. Thus the same empirical correlation used for the esters will presumably be applicable to a variety of corresponding MTPA amides of primary amines. The situation with respect to amides of secondary amines may be quite different, as shown by the proton nmr studies by Jacobus and Jones[7] and Helmchen.[8]

A configuration-correlation model has already been proposed for rationalizing the nonequivalence *proton* nmr spectra of MTPA diastereomeric esters.[4] This is shown in formulas **3A** and **3B** and **4A** and **4B** (Chart I).[9] No attempt was made to use models **4A** and **4B** to account for the $-CF_3$ chemical shift differences.[4] We now believe that the effect which leads to the nonequivalence of the α-CF_3 resonances in these diastereomers is an anisotropic deshielding of the α-CF_3 substituent by the ester carbonyl. Normally this might be a small effect, but, if other influential factors[10] are relatively constant between two diastereomers, then the anisotropic deshielding by the carbonyl group could be the determining factor responsible for the observed chemical shift differences. The magnitude of the observed ^{19}F diastereomer nonequivalence (up to 0.73 ppm) is in the range anticipated for such

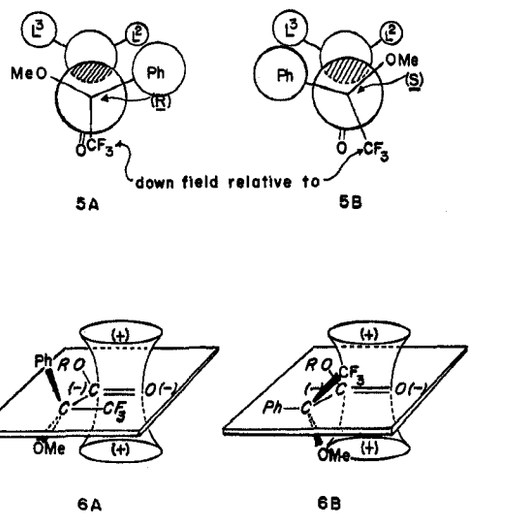
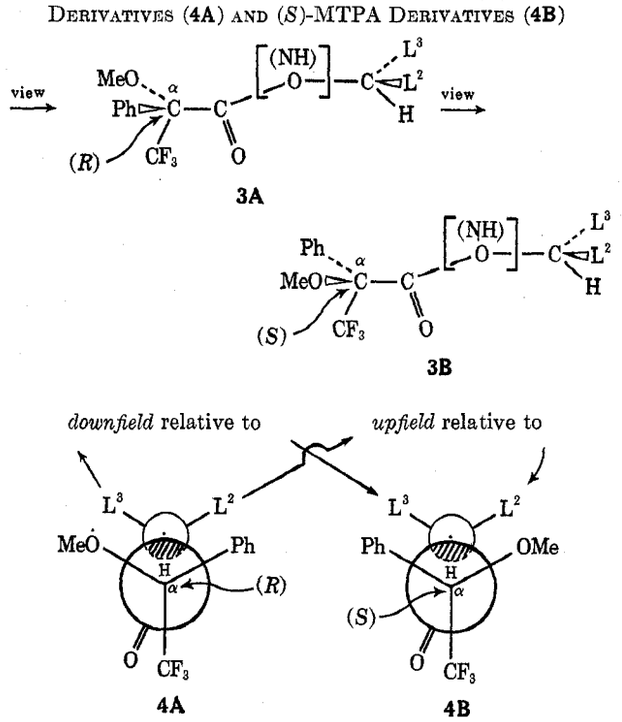


Figure 1.—Nmr ^{19}F configurational correlation models for diastereomeric MTPA derivatives. The cone-shaped field shown here is only an approximation; the carbonyl shielding environment is delineated more precisely in ref 12.

CHART I

CONFIGURATIONAL CORRELATION MODEL FOR (*R*)-MTPA DERIVATIVES (**4A**) AND (*S*)-MTPA DERIVATIVES (**4B**)



an effect[12] in which the α-CF_3 group finds itself either in a relatively deshielded environment (relatively downfield) as represented in **5A** or in a relatively more shielded environment (relatively upfield) as in **5B** (Figure 1). In these proposed models (**5A** *vs.* **5B**) the extent of deshielding of the α-CF_3 group will depend upon the extent that the α-CF_3 group is forced out of coplanarity by the interactions of L^2 and L^3 with the α-methoxy and phenyl groups. These interactions can be either steric, electronic, or both. The results are best rationalized by focusing on the α-phenyl group.

(6) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 36–37, 55–57, 89, 363.

(7) J. Jacobus and T. B. Jones, *J. Amer. Chem. Soc.*, **92**, 4583 (1970).

(8) G. Helmchen, private communication, University of Stuttgart, Germany.

(9) It has been previously emphasized[2,4] and should be restated that formulas **4A** and **4B** are intended to represent a model which successfully correlates the known results. These are not intended to represent the preferred ground state conformation of the molecules under consideration. They may in fact measure an effective average of many conformations or may represent a minor conformation which, however, exerts a proportionately large differential shielding of the L^2 and L^3 groups. Admittedly the success of the correlation tends to reinforce the belief that these do indeed represent major conformations of the molecules in question, but it must still be borne in mind that the possibility exists that this is a fortuitous array which happens to serve as an empirical correlation of the results.

(10) The paramagnetic contribution to the shielding of the fluorine nuclei is approximately 100 times that of the diamagnetic contribution and is responsible for the generally large variance observed for ^{19}F chemical shifts.[11] In the examples under consideration the α-CF_3 resonances are all found within a range of 2 ppm. It seems reasonable, therefore, to propose that the paramagnetic contribution within diastereomeric pairs is relatively constant and that the differences in α-CF_3 resonances observed between such pairs can result from diamagnetic inequalities in the environment caused by its orientation with respect to the carbonyl group as proposed here.

(11) (a) N. F. Ramsey, *Phys. Rev.*, **86**, 243 (1952); (b) J. W. Emsley, J. Feeroy, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1965, p 874.

(12) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 88–92.

Let us first assume (1) that the interactions with which we are concerned in the basic model represented by **5** are primarily steric in nature, (2) that phenyl is sterically more bulky than methoxyl, and (3) that L^3 is more bulky than L^2. Under these conditions, diastereomer **5A** should have the α-CF_3 group more nearly coplanar with the carbonyl group than diastereomer **5B**. In **5A** the steric interactions are minimized by $[(L^3||OMe) + (L^2||Ph)]$ with the larger substituent L^3 opposed to the smaller methoxy and the smaller L^2 opposed to the larger phenyl. In the alternate diastereomer **5B** the interactions will be $[(L^3||Ph) + (L^2||OMe)]$, which juxtapose the two large groups on one side and the two small groups on the other. The overall result should be a rotation (on the average) of the α-CF_3 group out of coplanarity with the carbonyl group in diastereomer **5B**. As a consequence, the diastereomer represented by **5B** should have the α-CF_3 group in a less deshielded environment of the carbonyl group as represented in **6B** and its resonance should be upfield relative to that in diastereomer **6A**.

The explicit use of this configuration-correlation model for prediction of configuration based on the ^{19}F nmr nonequivalence of MTPA diastereomers (with external TFA in $CDCl_3$ solvent) is as follows. That diastereomer prepared from (*R*)-(+)-MTPA with the downfield α-CF_3 signal relative to the α-CF_3 resonance of the alternate diastereomer will have configuration **5B** (equivalent to **3B**) where L^2 is sterically smaller than L^3. If (*S*)-(−)-MTPA is used in preparing the derivatives, then that diastereomer with the relatively downfield α-CF_3 resonance will be the enantiomer of **5B**. The configurational designation follows from application of the Cahn–Ingold–Prelog nomenclature rules.

This model clearly and simply rationalizes the α-CF_3 nmr data in Table I, with the exception of the MTPA esters of phenyl-*tert*-butylcarbinol, *n*-butyl-*tert*-butylcarbinol, isobutyl-*tert*-butylcarbinol, trifluoromethyl-*tert*-butylcarbinol, and borneol; these examples represent special cases requiring further consideration. The phenyl-*tert*-butylcarbinyl MTPA ester of known configuration follows the correlation model when L^2 is *tert*-butyl and L^3 is phenyl; *i.e.*, when phenyl is considered to be larger than *tert*-butyl. This is in accord with the most asymmetric synthesis;[6] therefore, it is the expected result, although the apparent relative sizes of phenyl and *tert*-butyl are not obvious.[13]

Correlation of the α-CF_3 nmr resonances of the *n*-butyl-*tert*-butylcarbinol and isobutyl-*tert*-butylcarbinol MTPA esters of known configuration requires that one consider for the purpose of this correlation scheme that *n*-butyl and isobutyl both act as though they are more bulky than *tert*-butyl. This is contrary to findings based upon asymmetric Grignard reductions.[14] However, the observation that asymmetric synthesis using *n*-butyl-*tert*-butylcarbinyl benzoylformate gives a reversal in stereoselectivity depending upon its reaction with either methyl Grignard reagent or lithium tri-*tert*-butoxyaluminohydride[15] emphasizes the complexity of the group size concept.[8] Certainly *tert*-butyl acts as the more bulky group in comparison to the *n*-butyl and isobutyl groups in those cases where the focus of steric interaction is located adjacent to these substituents (as in the asymmetric reduction of Me_3CCOR ketones). However, in cases where the prochiral reaction center is more remote from the inducing chiral center [as in the PhCOCOO-CHR(CMe_3) reactions][15] the longer *n*-butyl and isobutyl groups may be able to extend their influence to the remote carbonyl reaction center better than the shorter *tert*-butyl group. The present study of diastereomer differences in the α-CF_3 nmr resonances of MTPA derivatives must reflect conformational interactions resembling the situation which exists with the benzoylformate esters. Similar observations were made by Landor and coworkers[16] in asymmetric reduction of various ketones using the chiral lithium aluminum hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex.

It is unrealistic to hope to correlate interactions of electronegative groups such as phenyl and trifluoromethyl on steric grounds alone. The present data confirm this. In the MTPA esters of trifluoromethylphenylcarbinol, the group interactions for the two diastereomers represented by **5** are $[(CF_3||OMe) + (pH||Ph)]$ and $[(CF_3||Ph) + Ph||OMe)]$. An intuitive evaluation of the electronic and steric factors in this situation indicates that they are essentially equivalent and thus the rotation out of coplanarity for **5A** *vs.* **5B** would be minimal. This is in accord with the observation of no significant α-CF_3 nmr nonequivalence in these diastereomers.

However, when we consider the diastereomeric MTPA esters of trifluoromethyl-*tert*-butylcarbinol we find a different situation with the following interactions: $[(t\text{-Bu}||OMe) + (CF_3||Ph)]$ *vs.* $[(CF_3||OMe) + (t\text{-Bu}||Ph)]$. Previous asymmetric reduction studies[17] indicate that the $CF_3||Ph$ repulsive interaction is especially large, and we therefore conclude that the largest rotation out of coplanarity as represented in **5B** will be for that diastereomer in which L^3 is designated to be CF_3 and L^2 to be *tert*-butyl,[6] but it is altogether reasonable to postulate that electronic repulsions exert a dominant influence here. This interpretation is in accord with the published absolute configuration of trifluoromethyl-*tert*-butylcarbinol.[18] Thus the discrepancy in this case based upon steric interactions alone is successfully rationalized by taking electronic interactions into considerations.

The MTPA esters of menthol, cholesterol, and borneol represent examples in which the chiral alcohol moiety contains asymmetric centers other than the one to which the ester is bonded. In such cases it may be that one or more of these additional asymmetric centers is influential in determining the nmr nonequivalence. In spite of this, both the menthyl ester and

(13) For instance, the relative axial *vs.* equatorial conformational energy values for phenyl *vs.* *tert*-butyl in cyclohexane systems indicate that *tert*-butyl is substantially more bulky: J. A. Hirsch, *Top. Stereochem.*, **1**, 207 (1967). This is in contrast to the general experience in asymmetric synthesis studies.[6]

(14) See ref 6, pp 182–186.

(15) S. Yamaguchi, J. A. Dale, and H. S. Mosher, *J. Org. Chem.*, **37**, 9254 (1972).

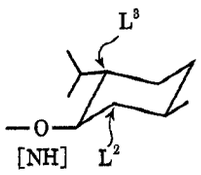
(16) S. R. Landor, B. J. Miller, and A. R. Tatchell, *J. Chem. Soc. C*, 2280 (1966).

(17) Reference 6, pp 190–193.

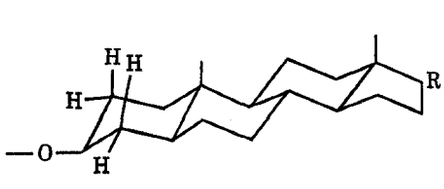
(18) The absolute configuration of trifluoromethyl-*tert*-butylcarbinol has not been proven unequivocally but has been deduced based upon reasonable correlations: H. Peters, D. M. Feigl, and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968).

the amide examples fit the general scheme of L^2 being smaller than L^3.

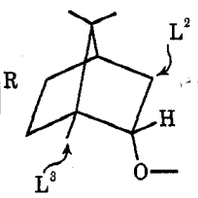
The carbinyl carbon in cholesterol (**7**) is flanked on each side by a methylene group; accordingly one might anticipate that there would be little difference in the α-CF_3 nmr resonances for these MTPA diastereomers. This is what we observe.



6, *l*-menthyl



7, cholesteryl



8, *d*-bornyl

However, we have checked both (−)- and (+)-bornyl MTPA esters and confirm that the *d*-bornyl ester with the *S* configuration at the carbinyl carbon shows the α-CF_3 resonance of the (*R*)-MTPA ester downfield with respect to that of the (*S*)-MTPA ester. In borneol the methylene group at C-2 is clearly designated L^2 (smaller) while the quaternary carbon at C-2 is L^3 (larger). Thus this lone example stands as a clear exception to the general correlation scheme for the α-CF_3 resonances.

Finally, the presence of heteroatoms in either L^2 or L^3, as in entries 6 and 7, Table I, may profoundly change the molecular conformations upon which the correlation is based. The fact that the correlation does hold in a case such as ethyl lactate does not necessarily mean that this will be generally so for all α-hydroxy esters. These examples must be taken only as indication that it may be possible to successfully extend the correlation to these types by further study.

Experimental Section

Instruments.—All ^{19}F resonance measurements were made on a Varian XL-100 nmr spectrometer[19] at 94.1 MHz using 5-mm nmr tubes, $CDCl_3$ solvent, and external trifluoroacetic acid (TFA) as standard. The TFA was contained in a sealed, precision ground, coaxial cell which was necked down at the bottom to a concentric 25 × 2 mm o.d. capillary stem containing the degassed TFA.

Reagent.—(+)-α-Methoxy-α-trifluoromethylphenylacetyl chloride, (+)-MTPA-Cl, was prepared from (*R*)-(+)-α-methoxy-α-trifluoromethylphenylacetic acid,[5] (*R*)-(+)-MTPA, according to the previously described method.[3c,4]

MTPA Derivatives.—The MTPA esters and amides were prepared from (+)-MTPA-Cl according to the previously described procedure.[4] Two derivatives were usually prepared, one from enantiomerically pure carbinol and amine and (+)-MTPA-Cl and a second using MTPA-Cl which was about 70% (+)-MTPA-Cl and 30% (−)-MTPA-Cl. This permitted the unequivocal establishment of the nmr chemical shift for each diastereomer.

Chiral Carbinols and Amines.—These compounds were available from previous studies in these laboratories by the methods indicated by the references to Table I.

Acknowledgment.—We are grateful to Dr. Lois Durham, Director of the Stanford Chemistry Department Nmr Laboratories, for her continued help and cooperation.

(19) We gratefully acknowledge Grant GP 28142 from the National Science Foundation to the Stanford Chemistry Department for the purchase of this instrument.

The 2:1 Adduct from Diphenylketene and 1,1-Diphenylethylene. 3,4-Dihydro-1,4,4-triphenyl-2-naphthyl Diphenylacetate[1,2]

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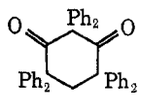
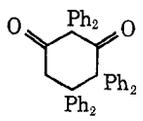
The 2:1 adduct from the thermal reaction of diphenylketene and 1,1-diphenylethylene has been conclusively identified as 3,4-dihydro-1,4,4-triphenyl-2-naphthyl diphenylacetate, and part of the degradation of the adduct reported in 1958 by Farooq and Abraham has been repeated and reinterpreted.

The 2:1 adduct derived from the reaction of diphenylketene with 1,1-diphenylethylene at 150° was first obtained by Staudinger and Suter[3] in 1920. Their original structural proposal, 2,2,4,4,6,6-hexaphenylcyclohexane-1,3-dione (**1**), was revised by Farooq and Abraham[4] in 1958 to 2,2,4,4,5,5-hexaphenylcyclohexane-1,3-dione (**2**).



1



2

The later proposal was bolstered by results obtained through a degradation of the 2:1 adduct, a degradation which led eventually to some 1,1,4,4-tetraphenyl-1-butene, claimed to be identical with an authentic, independently synthesized sample of this hydrocarbon. Salient features of degradation are outlined in Scheme I.

In the course of a thorough kinetic investigation of the cycloaddition reaction between diphenylketene and 1,1-diarylethylenes[5] we secured infrared and nmr spectral data on five adducts of this class. These data were inconsistent with cyclohexanedione structural postu-

(1) Supported by the National Science Foundation and Hoffmann-La Roche Inc.

(2) A preliminary account of this work has appeared: J. E. Baldwin, M. F. Breckinridge, and D. S. Johnson, *Tetrahedron Lett.*, 1635 (1972).

(3) H. Staudinger and E. Suter, *Ber. Deut. Chem. Ges.*, **53**, 1092 (1920).

(4) M. O. Farooq and N. A. Abraham, *Bull. Soc. Chim. Fr.*, 832 (1958).

(5) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **92**, 4868 (1970).