Neighboring-Group Effects on the Proton Chemical Shift of the *tert*-Butyl Group. Rotational Conformations in the Diastereomers of 1,3-Di-*tert*-butylpropargyl 2-Phenylpropionate

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The proton nmr spectra of 1,3-di-*tert*-butylpropargyl alcohol (1) and 11 derivatives and *tert*-butyl-containing model compounds have been examined in an attempt to assign the chemical shifts of the two *tert*-butyl resonances in 1. It was found that, in the absence of "special effects," the ethynyl *tert*-butyl absorption (EBu) fell at lower field (δ 1.23 ± 0.02) than the alkyl *tert*-butyl resonance, ABu (δ 0.97 ± 0.03), in these compounds, and this has been interpreted as an experimental determination of the shielding and deshielding regions surrounding the triple bond. The "special effects" include long-range shielding by a benzene ring, which is manifested in the tosylate of 1 and in 2,4,4-trimethyl-2-(*p*-hydroxyphenyl)pentane. The reaction of 1 with 2-phenylpropionoyl chloride (7) in pyridine led to a mixture of two (enantiomeric pairs of) diastereomers of 1,3-di-*tert*-butylpropargyl 2-phenylpropionate (8) in nearly equal amounts. One of these (pairs), A, has a normally positioned ABu and a shielded EBu, while the other (B) has a normal EBu and a shielded ABu. The reaction of (*R*)-(+)-1 with (*S*)-(+)-7 (both of known enantiomeric purity) led to (*RS*)-(+)-8, which was identified with B. Thus the *RR*, *SS* pair corresponds to A. A simple statistical model that allows calculation of relative amounts of each of the four stereoisomers produced in such a reaction is presented and found to give reasonable agreement with experiment. The differences in the pmr spectra of A and B are explained on the basis of opposite preferences in the rotational conformations of A and B allowing, on the time average, selective shielding of the EBu in A and the ABu in B by the remote aromatic ring.

During the course of our studies involving the 1,3-di-*tert*-butylpropargyl system[1,2] it became necessary to unambiguously assign the *tert*-butyl resonances in the proton nmr spectrum of 1,3-di-*tert*-butylpropargyl alcohol (1).[1-3] One approach to the problem seemed to be comparison of the chemical shifts found for 1 with those of similarly constituted model compounds, but unfortunately few such data were available in the literature. Thus we undertook measurements on several known and some new compounds, the results of which are presented, together with several literature values, in Table I. The chemical shifts of the *tert*-butyl resonances in these compounds were, as expected, quite insensitive to concentration and nature of the solvent (less than 0.03 ppm upon changing from deuteriochloroform to carbon tetrachloride) in support of the meaningfulness of these comparisons.

It is immediately tempting to assign the higher field resonance of 1 (δ 0.95) to the alkyl *tert*-butyl group (ABu) and the lower field absorption (δ 1.22) to the ethynyl *tert*-butyl group (EBu), because the latter matches the value for *tert*-butylacetylene, which in turn is 0.28 ppm to lower field than that of neopentane. Substitution of an acetoxy group (2) for the hydroxyl in 1 has essentially no effect on the ABu and EBu chemical shifts, an observation that will become important later. The methyl-bearing derivative (3) of 1 further serves to establish the trends in chemical shifts: the EBu absorptions occur at δ 1.23 ± 0.02, while ABu falls in the region δ 0.97 ± 0.03. Tri-*tert*-butylpropargyl alcohol (4) unambiguously confirms the $\delta_{\mathrm{EBu}} > \delta_{\mathrm{ABu}}$ ordering with an 18-proton singlet at δ 1.13[4] and a 9-proton singlet at δ 1.24.

The assignment $\delta_{\mathrm{EBu}} > \delta_{\mathrm{ABu}}$ has a further consequence. Induced diamagnetic electron circulation in the carbon–carbon triple bond is believed to account for the *shielded* nature of acetylenic protons and presumably other groups situated *on or near* the internuclear axis of the triple bond. However, comparison of the second and fourth entries in Table I would suggest that an EBu is *deshielded* by *ca.* 0.25 ppm with respect to a saturated analog (*e.g.*, the ABu). This enables one to experimentally locate the "lines" of induced magnetic flux density surrounding the triple bond in such a way that the *tert*-butyl protons experience, on the time average, a net *deshielding* effect (Figure 1). This model can be contrasted with the results of semiempirical calculations. An early approach,[5] which treated the triple bond as a point dipole located at the midpoint of the bond, suggested that the volume surrounding the triple bond be bifurcated into shielding (+) and deshielding (−) regions as shown by the dashed lines in Figure 1. More recently Pople and Untch[6] used a model which locates point dipoles at each end of the triple bond, giving rise to eq 1.

$$\Delta\sigma = \Delta\chi \sum_{n} \frac{1-3\cos^2\theta_n}{3R_n^3} \qquad (1)$$

Clearly the former treatment incorrectly predicts that the EBu protons should lie within the shielding region. A calculation with eq 1 using values[6] of $\Delta\chi = -1.96 \times 10^{-5}$ Å^3, $R_1 = 2.78$ Å, $\theta_1 = 140°$, $R_2 = 3.80$ Å, and $\theta_2 = 151.5°$ (these values representing the rotationally averaged position of the EBu protons, shown by the asterisk in Figure 1) also predicts a 0.39-ppm shielding effect, again in contrast to our observation. It seems quite unlikely that the observed deshielding could result from a long range effect of the electronegative sp-hybridized carbon atom. Intermediate between an acetylenic proton and those in an EBu is the situation of a methyl group attached to a triple

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(1) R. S. Macomber, *Tetrahedron Lett.*, 4639 (1970).

(2) R. S. Macomber, *J. Org. Chem.*, **36**, 2713 (1971).

(3) E. J. Corey and W. T. Borden, *Tetrahedron Lett.*, 313 (1969).

(4) The downfield shift of the ABu absorptions in **4** can be attributed in part to the increased *s* character in the *C-tert*-butyl bonds caused by the "spreading" steric interaction between the two geminal *tert*-butyl groups, and in part to the movement of the ABu groups into the deshielding region of the triple bond (*vide infra*).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(6) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966). The value given here for $\Delta\chi$ (-11.8×10^{-6} cm^3/mol) is equivalent to the one used in the present calculations.

TABLE I

CHEMICAL SHIFTS OF THE *tert*-BUTYL RESONANCES OF **1** AND MODEL COMPOUNDS[a]

Compound	Solvent	ABu	EBu	Ref
tert-BuC≡C—CHOH-*tert*-Bu (**1**)	CCl_4 ($CDCl_3$)	0.95 (0.97)	1.22 (1.22)	*b*
$(CH_3)_4C$		0.94		*c*
tert-BuCH_2OH	CCl_4	0.88		*b*
tert-BuC≡CH	CCl_4 (neat)		1.22 (1.22)	*b*
tert-BuC≡CH($OCOCH_3$)-*tert*-Bu (**2**)	CCl_4	0.95	1.21	*d*
tert-BuC≡CC(OH)(CH_3)-*tert*-Bu (**3**)	CCl_4	1.00	1.22	*e*
tert-BuC≡CC(OH)(*tert*-Bu)$_2$ (**4**)	CCl_4	1.13	1.24	*f*
tert-BuC≡CCH(OTs)-*tert*-Bu (**5**)	CCl_4	1.00	1.00	*b*
p-$HOC_6H_4C(CH_3)_2CH_2$-*tert*-Bu	$CDCl_3$	0.72		*g*
A	CCl_4	0.92	1.13	*b*
B	CCl_4	0.79	1.21	*b*
o-$HOOCC_6H_4CO_2CH$(*tert*-Bu)C≡C-*tert*-Bu	CCl_4	1.05	1.25	*b*

[a] Shift values (60 MHz) in parts per million downfield from internal TMS. [b] Present study. [c] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959. [d] Reference 1. [e] This compound was prepared in our laboratories using a published procedure: A. I. Zehkarova and G. M. Murashov, *Zh. Obshch. Khim.*, **23**, 1981 (1953). [f] The full details of the synthesis of this compound will appear later in connection with another study. [g] Varian Associates, "High Resolution NMR Spectra Catalog," spectrum 315.

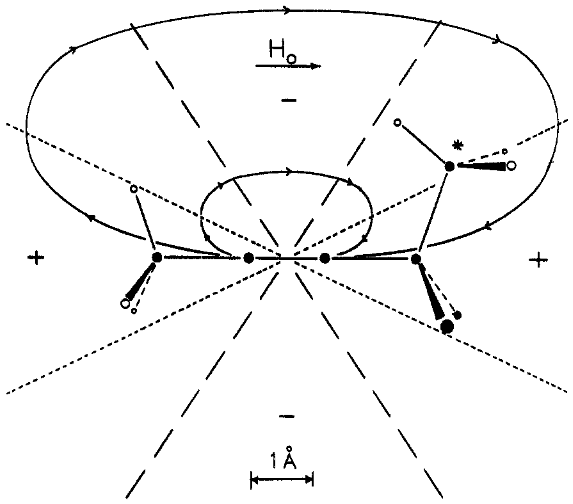
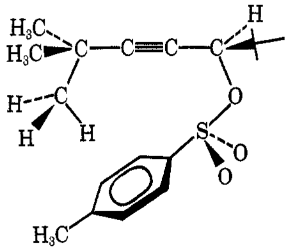


Figure 1.—Geometric model for the shielded (+) and deshielded (1) regions surrounding a carbon–carbon triple bond substituted on the left with a methyl group and on the right by a *tert*-butyl group. ● = carbon, ○ = hydrogen; bond lengths and angles are scaled to published values (J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968). Dashed lines show the previously calculated regions;[5] dotted lines demarcate the experimentally verified regions. The asterisk locates the average position of the EBu protons.

bond, which appears at δ 1.80,[7] reflecting *net* deshielding. It is difficult to say whether this results from long range *deshielding* by the triple bond, through bond deshielding by the sp carbon atom, or the latter effect coupled with compensating *shielding* by the triple bond. Equation 1 predicts a shielding contribution of 0.69 ppm, but this would require through-bond sp deshielding of 1.6 ppm to account for the observed resonance at 1.80. Our model places the methyl protons very near the lines separating the shielded and deshielded regions (dotted lines in Figure 1). It is perhaps also significant that the ABu in **1** occurs 0.07 ppm to lower field than the ABu in neopentyl alcohol. This too may be due to triple bond deshielding in the former, but the magnitude of the effect is too small to be unequivocal.

With the chemical shift assignments secure, the situation appeared relatively simple until we found that with 1,3-di-*tert*-butylpropargyl tosylate[1,3] (**5**, Table I) *both tert*-butyl resonances occur exactly at δ 1.00! This suggests that the remote aromatic ring spends a significant fraction of its conformational time near enough to the EBu that the *deshielding* effect of the triple bond is exactly compensated by the *shielding* influence of the face of the benzene ring. Such long range shielding effects are not without precedent,[5] as shown by the ninth entry in Table I.



In order to assess the generality and limitations of these types of interaction we chose to prepare derivatives of **1** similar in nature to **5** with remote phenyl substituents. The most significant results arose from the reaction of **1** with 2-phenylpropionic (hydratropic) acid **6** (*via* the acid chloride, **7**). Because both **1** and **6** possess a center of chirality it was likely that the reaction would lead to a mixture of (enantiomeric pairs of) diastereomers, but preliminary examination of space-filling molecular models did not permit a decision as to which pair might be preferentially formed or, once formed, if they would be easily separable on steric grounds. Reaction of **1** with an equimolar amount of **7** in pyridine led, in 81% yield, to a high boiling oil with the composition of the anticipated ester(s) 1,3-di-*tert*-butylpropargyl 2-phenylpropionate (**8**). After several unsuccessful attempts, the oil was ultimately resolved by glpc on a Carbowax 20M column and shown to be a mixture of two components, A and B (in the order of their elution), in the ratio 48.6:51.4%. Although the ir spectra of the two compounds were virtually identical, the proton nmr spectra (Experimental Section) differed significantly in the *tert*-butyl regions (Table I). Comparison of these values with the previously considered ones suggested that diastereomer A had an essentially "normal" ABu and a significantly (0.10 ppm) *shielded* EBu, while isomer B had

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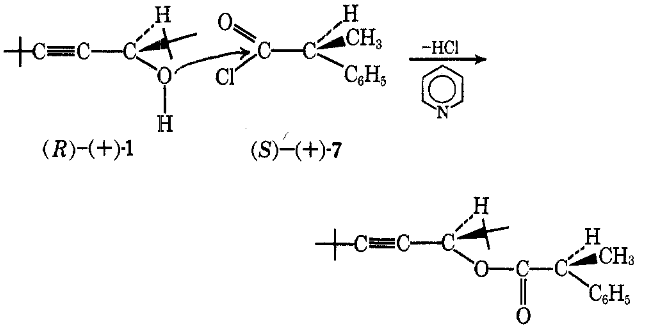
[7] Varian Associates, "High Resolution NMR Spectra Catalog," Spectrum No. 16.

a normal EBu and a significantly (0.18 ppm) *shielded* ABu!

In order to ascertain the absolute configuration of the diastereomers, we proceeded to resolve the reactants using published procedures. Acid **6** was resolved by means of its strychnine salt[8-10] to yield (*S*)-(+)-**6**, $[\alpha]^{24.3}\mathrm{D}$ +85.8° (*c* 3.48, benzene), which corresponds to an optical purity[11] of 92.8% and an enantiomeric purity of 96.4%. (*S*)-(+)-**6** was converted to the acid chloride, (*S*)-(+)-**7**, with thionyl chloride, the product having $[\alpha]^{24.8}\mathrm{D}$ +74.2° (*c* 2.83, chloroform).[12] Alcohol **1** was resolved *via* the brucine salt of its phthalate half ester[3] to yield (*R*)-(+)-**1**, $[\alpha]^{24.5}_{578}$ +4.66° (*c* 1.310, chloroform), which indicates an optical purity of 97.0% and an enantiomeric purity of 98.5%.[14]

Scheme I



(*R*)-(+)-**1** (*S*)-(+)-**7**

(*RS*)-(+)-**8**

The product from the resolved reactants should then be nearly pure (*R*)-1,3-di-*tert*-butylpropargyl (*S*)-2-phenylpropionate [(*RS*)-**8**]. But how nearly pure? A fairly simple statistical analysis can be developed to estimate the relative amounts of all four stereoisomers of **8**, given the enantiomeric purity of **1** (x), the enantiomeric purity of **7** (y), and the factor (f) by which the major diasteromer is favored over the minor diastereomer *under racemic conditions*. Provided we start with equimolar amounts of **1** and **7** and addition of reactants is much faster than the reaction itself, the relative amount of a given diastereomer, for example *RS*, should be determined by the relative probability of finding an (*R*)-**1** molecule (x) times the relative probability of finding an (*S*)-**7** molecule (y) multiplied by the favoring factor f. Thus if the *RS* and *SR* diastereomers were the favored ones (*vide infra*) the relative amounts would be given by

$$\begin{aligned}\%\ (RS)\text{-}\mathbf{8} &= 100xyf/N\\ \%\ (SR)\text{-}\mathbf{8} &= 100(1-x)(1-y)f/N\\ \%\ (RR)\text{-}\mathbf{8} &= 100x(1-y)(1-f)/N\\ \%\ (SS)\text{-}\mathbf{8} &= 100(1-x)y(1-f)/N\end{aligned}$$

where N, the normalization factor, is given by

$$N = (2f-1)(2xy-x-y)+f$$

Using the values $x = 0.985$, $y = 0.964$, and $f = 0.514$, (*vide supra*), the predicted amounts, assuming no mechanical or optical loss, are

$$\begin{aligned}\%\ (RS)\text{-}\mathbf{8} &= 95.3\\ \%\ (SR)\text{-}\mathbf{8} &< 0.1\\ \%\ (RR)\text{-}\mathbf{8} &= 3.3\\ \%\ (SS)\text{-}\mathbf{8} &= 1.4\end{aligned}$$

Because the glpc separation will not distinguish enantiomers, we would expect to observe one peak [(*RS*)- + (*SR*)-**8**] comprising 95.3% of the product and another [(*RR*)- + (*SS*)-**8**] comprising 4.7%.

When the reaction mixture was analyzed under the same conditions as for the racemic materials, two components emerged, the first (A) constituting 4.0%, the second (B) constituting 96% in excellent agreement with the expectation! Thus the *RS* and *SR* stereoisomers can be identified with B (Table I) while the *RR* and *SS* isomers correspond to A. The mixture had $[\alpha]^{25}\mathrm{D}$ +86.2° (*c* 1.614, chloroform).

Before correlating the absolute configuration with proton nmr behavior in **8**, several facts should be noted. Although the ratio of A to B is near unity, it is significantly dependent on reaction conditions. The two experiments above involved addition of a pyridine solution of **1** to a cooled sample of **7** and stirring from 0 to 25° for 2.5 hr. It was found, however, that addition of **1** to a solution of excess **7** in pyridine at room temperature and stirring for 14 hr led in ~79% yield to a mixture with ratio 60:40 (A:B). One possible explanation was that pyridine served to promote an enolization epimerization[13] (*RS* → *RR*, *SR* → *SS*) of **8**, but this was ruled out by the observation that the diastereomer ratio (A:B) was unchanged after 11.5 hr in pyridine. Another likely explanation would invoke the formation of a pyridinium complex with **7** under the second set of conditions and that this intermediate had different steric requirements than uncomplexed **7**. One might also argue that the less than quantitative yields (80–85%, but see Experimental Section) make the data a little difficult to interpret, but the close correspondence between the calculated and observed amounts of the two diastereomers (*vide supra*) suggest that, if some loss or destruction of esters occurs during work-up, there is little or no selection between the diastereomers. At any rate the above data taken *in toto* verify that the published specific rotations for optically pure **1** and **6** are correct,[3,8-14] as is the above procedure for estimation of stereoisomer populations.

Returning to a discussion of the nmr spectra, why is the *ABu* in (*RS*)- [and (*SR*)-] **8** shielded, while it is the *EBu* in the *RR* and *SS* isomers that is shielded? The explanation cannot be a simple function of the adjacent ester linkage in **8**, for, as we have already seen, going from **1** to **2** has no measurable effect on the chemical shifts of either *tert*-butyl group. We feel that the observations are best explained by examining the rotational conformations available in the two diastereomers.

If we consider two of the diastereomers, the *RS* and the *RR*, it is immediately clear that the differentiating

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[8] C. L. Arcus and J. Kenyon, *J. Chem. Soc.*, 916 (1939).

[9] F. A. Abd Elhafez and D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 5846 (1952).

[10] B. Sjoberg, *Ark. Kemi*, **13**, 1 (1959).

[11] In determining these purities we used the value $[\alpha]^{25}\mathrm{D}$ +92.5° (*c* 3.4825, benzene)[8] which corresponds to $[M]^{25}\mathrm{D}$ +138.8° (benzene)[10] for optically pure (*S*)-(+)-**6**.

[12] Although one can visualize ready racemization of **6** and **7** *via* acid- or base-catalyzed enolization, the assumption seems to have been made that formation of (*S*)-(+)-**7** from (*S*)-(+)-**6** entails no loss of optical purity.[8,9] This has been experimentally verified by the observation that **6**, converted to **7** then hydrolyzed back to **6**, showed only a 3% loss in optical rotation.[13] We have assumed no loss in optical purity during our preparation of the chloride, and thus the specific rotation of (*S*)-(+)-**7** can be estimated to be $[\alpha]^{28.8}\mathrm{D}$ +79.9° (*c* 2.83, chloroform).

[13] J. Smejkal and J. Farkas, *Collect. Czech. Chem. Commun.*, **28**, 481 (1963).

[14] It should be noted that (+)-**1** was previously[3] given the incorrect designation *S*, while the isomer shown there and in Scheme I should carry the designation *R*, as the *tert*-butylethynyl group has precedence by complementation, over a *tert*-butyl group.[15]

[15] E. L. Eliel, private communication.

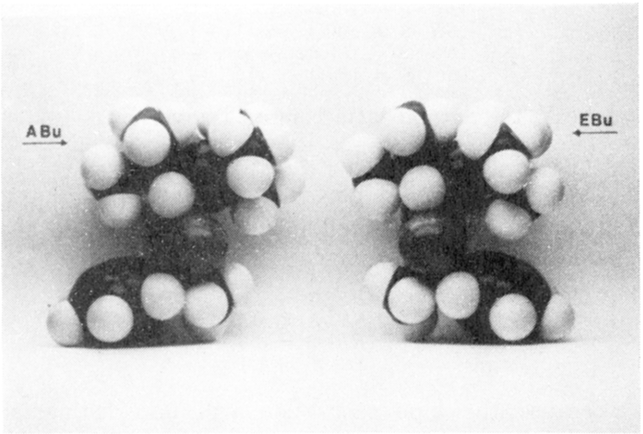
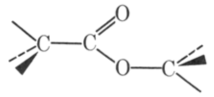


Figure 2.—Space-filling molecular models of (*RS*)-**8** (left) and (*RR*)-**8** (right). Notice the mirror-image relationship of the acid fragments and the similar configuration of the alkoxy residues.

factor(s) must intimately involve the methyl groups on the acid residues, for if they were replaced by hydrogen both molecules would be identical. Careful consideration of space-filling models of the diastereomers shows that both are relatively bulky and free rotation of most single bonds is limited. Two factors appear dominant in assuring minimized nonbonded repulsions throughout the molecules: first is the desire for one of the ortho hydrogens on the phenyl ring to be nestled between the methyl and carbonyl oxygen of the acid moiety, and second is the selection of the *s-trans* conformation of the ester linkage.



Given these two constraints, it is fairly easy to see that in (*RS*)-**8** the ABu can be brought, without significant increase in conformational energy, into the shielding region of the benzene ring,[16] while steric buttressing prevents free rotation of the alcohol fragment in such a way as to bring the EBu into the shielding zone. The situation with the *RR* stereoisomer is just reversed; the conformation with the EBu over the ring is favored, while one which places the ABu in the shielding region possesses considerable nonbonded interactions throughout the molecule. Further evidence for these conclusions can be adduced from the fact that the more distended diastereomer (the *RS*) also has the longer glpc retention time. Molecular models (Figure 2) clarify these situations. These findings further confirm the correctness of the *R*[14] configuration of (+)-**1**. One final interesting observation is the apparent absence of shielding influence by the benzene ring in the phthalate half ester of **1** (Experimental Section), with ABu at δ 1.05 and EBu at δ 1.25. This can be explanied by the fact that no conformation exists which simultaneously allows either *tert*-butyl group to pass over the aromatic ring while maintaining conjugation between the ring and the C=O.

To summarize, it appears that the *tert*-butyl chemical shift is a relatively sensitive probe of molecular stucture. In the absence of "special effects" an alkyl *tert*-butyl group will fall into the region of δ 0.97. Special effects include attachment to a triple bond, which has a deshielding influence (δ 1.23), and the possibility of rotation into the shielding region of an aromatic ring.[17,17a]

Experimental Section

General.—The following instruments were employed: pmr spectra, Varian A-60; optical rotations, Cary 60 in ORD mode; ir spectra, Perkin-Elmer Model 700; mass spectra, Hitachi RMU 7 operated at 70 eV; glpc, Hewlett-Packard Model 700 equipped with TC detector and fitted with an 8 ft × $^1/_8$ in. column packed with 12% Carbowax 20M on 80/100 Chromosorb W, AW-DMSC (column temperature 140°, injection block 159°, detector 160°, flow rate 30 ml/min). Quoted glpc percentages were derived from disc-integrated peak areas and are not corrected for response factor differences, which should be small for diastereomers A and B; these percentages were reproducible to ±0.2%. Elemental analyses were performed by Chemalytics, Tempe, Ariz.

1,3-Di-*tert*-butylpropargyl alcohol (**1**) was prepared by the published procedure.[1,3] Resolution[3] of **1** was initiated by esterifying **1** with phthalic anhydride in pyridine[18] to yield the half ester: mp 112.5–113°; ir (carbon tetrachloride solution) 2260 1725, 1700, 1600, 1580, 1280 cm^{-1}; pmr (carbon tetrachloride, internal TMS) δ 13.17 (s, 1 H), 7.6 (br m, 4 H), 5.30 (s, 1 H), 1.25 (s, 9 H), 1.05 (s, 9 H). The brucine salt of the phthalate half ester was recrystallized four times from 80% aqueous acetone to yield a salt with $[\alpha]^{25}\mathrm{D}$ −13.4° (c 0.911, acetone). This material gave (*R*)-(+)-**1**, mp 58.5–60.0° (lit.[3] 58.8–60.3°) and rotation given in the text.

2-Phenylpropionic acid (**6**) was prepared in 69% yield by silver oxide oxidation of 2-phenylpropionaldehyde.[19] This material had bp 104–105° (1.0 mm) [lit.[19] 144–147° (11 mm)]; ir (carbon tetrachloride) 3000 (very broad), 1705, 1603 cm^{-1}; pmr (carbon tetrachloride, internal TMS) δ 12.04 (s, 1 H), 7.28 (br s, 5 H), 3.67 (q, J = 7 Hz, 1 H), 1.47 (d, J = 7 Hz, 3 H).

Five recrystallization of the strychnine salt from 75% aqueous ethanol yielded the salt with $[\alpha]^{25}\mathrm{D}$ −29.2° (*c* 0.896, ethanol). The (*S*)-(+)-acid isolated therefrom, mp 29–30° (lit.[8] 29°), had specific rotation given in text.

2-Phenylpropionoyl chloride (**7**) was prepared in 89% yield by use of thionyl chloride.[20] This material had bp 80° (4 mm) [lit.[20] 100–101° (13 mm)]; pmr (carbon tetrachloride, internal TMS) δ 7.31 (br s, 5 H), 4.06 (q, J = 7.3 Hz, 1 H), 1.53 (d, J = 7.3 Hz, 3 H).

When the reaction was carried out with acid of $[\alpha]^{24.3}\mathrm{D}$ +85.8°

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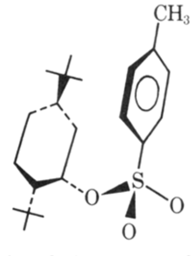
(16) The upfield shifts caused by the aromatic ring are of the magnitude (~0.15 ppm) expected for protons whose (time-averaged) location rests at p (the in-plane distance from the center of the ring) = 2.8 Å, and z (normal distance from center of ring) = 5.6 Å: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, Appendix B.

(17) For recent examples on the use of chemical shift in elucidating rotational preferences, see G. Montaudo, *et al.*, *J. Amer. Chem. Soc.*, **93**, 4202, 4208 (1971).

(17a) NOTE ADDED IN PROOF.—A recent X-ray study [D. H. Faber and C. Altona, *Chem. Commun.*, 1210 (1971)] has revealed that the *p*-toluenesulfonyl group in *cis,trans*-2,5-di-*tert*-butylcyclohexyl tosylate adopts a folded conformation in the crystalline state as shown. To the extent that



this conformation persists in solution, one would expect from the results described herein that the 5-*tert*-butyl group would experience net shielding by the aromatic ring while the 2-*tert*-butyl group should be unaffected. Professor Pasto [D. J. Pasto and D. R. Rao, *J. Amer. Chem. Soc.*, **92**, 5151 (1970)] has informed us that the *cis,trans*-tosylate exhibits two *tert*-butyl resonances, one at δ 0.89 (a normal value), the other at 0.667 (shielded by ~0.3 ppm), exactly in accord with expectation. Of course the possibility that the 2-*tert*-butyl becomes the shielded one in solution cannot at this point be excluded, but clearly one of the groups is significantly shielded while the other is not.

(18) For details of a similar resolution, see T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967).

(19) E. L. Eliel and J. P. Freeman, *ibid.*, **74**, 923 (1952).

(20) R. Delaby, P. Reynaud, and F. Lilly, *Bull. Soc. Chim. Fr.*, 2067 (1961).

(*c* 3.48, benzene) the product, (*S*)-(+)-**7**, had specific rotation given in the text.

Reaction of 1 with 7.—A solution of 998.8 mg (5.89 mmol) of **1** in 5 ml of dry pyridine was added rapidly, with magnetic stirring to 990.6 mg (5.88 mmol) of **7** cooled to 0° by means of an ice bath. Reaction, as gauged by the appearance of pyridine hydrochloride, was immediate. The reaction mixture, protected from moisture, was stirred for 2.5 hr, while the temperature climbed from 0 to 25°. The solution was poured over an equal volume of ice and extracted with ether (five 8-ml portions), which was then washed repeatedly with 1 *N* sulfuric acid until all pyridine had been removed, and once with saturated sodium chloride solution. The ether solution was dried, then rotary evaporated, leaving 1418.1 mg (81%)[21] of the product as an oil which did not freeze above −20°. Glpc showed two components, one at 8.4 min (48.6%) and one at 9.8 min (51.4%). Distillation gave an analytically pure mixture, slightly enriched in A, the lower boiling isomer (ratio of A to B 51:49), bp 88-91° (0.2 mm); *m/e* 300; ir (carbon tetrachloride) 2970, 2275, 1730, 1605, 1165 cm^{-1}. The pmr spectrum (carbon tetrachloride, internal TMS) clearly showed two sets of absorptions, the relative isomer distributions from which corresponded to within 1% of the ratio found with glpc. Isomer A: δ 7.27 (br s, 5 H), 5.05 (s, 1 H), 3.69 (q, J = 7.3 Hz, 1 H), 1.48 (d, J = 7.3 Hz, 3 H), 1.13 (s, 9 H), 0.92 (s, 9 H); Isomer B: δ 7.27 (br s, 5 H), 5.08 (s, 1 H), 3.68 (q, J = 7.3 Hz, 1 H), 1.48 (d, J = 7.3 Hz, 3 H), 1.21 (s, 9 H), 0.79 (s, 9 H).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.76; H, 9.41.

When the reaction was carried out with the resolved materials, the product, isolated in 86%[21] yield, gave an ir spectrum virtually superimposable on that of the diastereomer mixture (*vide supra*). This material, predominantly (*RS*)-(+)-**8**, did solidify to a glass at 0°, and remelted at ~30°; its specific rotation is given in the text. The pmr spectrum of the product was identical with that of B above, with *ca.* 5% of A discernible. Glpc showed a ratio of 4.0:96.0 (A:B). A 198-mg sample of racemic ester mixture was dissolved in 2 ml of dry pyridine and allowed to stand for 11.5 hr at ambient temperature. Work-up as above and then glpc analysis showed that the constitution of the mixture had changed by less than 2%.

Registry No.—**1**, 22688-43-3; **1** phthalic half ester, 33122-22-4; **1** phthalic half ester brucine salt, 33069-02-2; **6**, 7782-24-3; **6** strychnine salt, 33069-04-4; **7**, 25145-43-1; *R*,*R*-**8**, 33069-06-6; *S*,*S*-**8**, 33069-07-7; (+)-*R*,*S*-**8**, 33069-08-8; *S*,*R*-**8**, 33122-23-5.

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[21] It is significant to note that although isolated yields are somewhat less than quantitative, glpc analysis of the crude product mixtures showed unreacted **1** as the only contaminant.

Magnetic Circular Dichroism Investigations of Some Conjugated Olefins[1,2]

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The magnetic circular dichroism (MCD) curves of 12 conjugated dienes are reported. The series studied includes both acyclic and cyclic *s-cis-* and *s-trans*-dienes as well as compounds having a large range in skew angle values. From the lack of variation in the signs and magnitudes of the B/D values measured for the dienes studied, it is concluded that MCD, in the 200–300-nm region, has no distinct advantage over absorption spectroscopy for the structural identification of different diene systems. 1,3,5-Cycloheptatriene exhibits a more complex MCD spectrum than anticipated.

Magnetic circular dichroism (MCD) and magnetic optical rotatory dispersion (MORD) have been useful tools in the investigation of molecular structure[1] and in some cases have been found to be more sensitive to molecular structrual differences than either CD or ORD.[5] MCD has also been used to clarify spectroscopic assignments, detect hidden transitions, and characterize the symmetry and angular momentum properties of molecules in their ground and excited states.[6] The most important advantage of MCD is that it can be applied to optically inactive or racemic material.

A resurgence of interest during the past several years is clearly in evidence.[1] The impetus for this renewed interest comes primarily from Buckingham and Stephens' theoretical treatment of magnetic optical activity within absorption bands.[6a] The magnetic molar ellipticity, $[\theta]_{\mathrm{M}}$, associated with an isolated electronic transition $a \rightarrow j$, can be expressed by eq 1.[6b] In this

$$[\theta_{(a \rightarrow j)}]_{\mathrm{M}} = -21.3458 \, \{f_1 \mathrm{A}_{(a \rightarrow j)} + f_2[\mathrm{B}_{(a \rightarrow j)} + \mathrm{C}_{(a \rightarrow j)}/kT]\} \tag{1}$$

equation, the B term results from the mixing of energy levels by the magnetic field and is present for all molecules. The A and C terms result from Zeeman splitting of degenerate levels by the external field, and nonzero values for these magnetic rotational strengths will be oberved only for highly symmetrical molecules. The B and C terms are described by the same shape function, f_2, and have the bell shape characteristic of an absorption band. The curve observed for the A term, described by f_1, is the resultant of two oppositely

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[1] Part XVI in the series Magnetic Circular Dichroism Studies. For part XV, see C. Djerassi, E. Bunnenberg, and D. L. Elder, *Pure Appl. Chem.*, **25**, 57 (1971), a review of the applications of MCD in organic chemistry.

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[5] (a) W. Voelter, G. Barth, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 6165 (1969); (b) W. Voelter, R. Records, E. Bunnenberg, and C. Djerassi, *ibid.*, **90**, 6163 (1968).

[6] (a) A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966); (b) P. N. Schatz and A. J. McCaffery, *Quart. Rev., Chem. Soc.*, **23**, 552 (1969), and references cited therein.