by using gas chromatographic analysis of the collected pyrolysate containing *n*-decane as an internal standard. At higher temperatures, **4** was found to give a 1,3-disilacyclobutane product, as expected from earlier studies.[18]

Acknowledgment. This work was supported in part by Grant No. CA-19203 awarded by the National Cancer Institute, DHEW. The help of Professor P. J. Kocienski in obtaining the mass spectral data is gratefully acknowledged. The assistance of Mr. Ben Belinka in the preparation of analytical samples was much appreciated.

Registry No. 1A, 72301-23-6; 1B, 72301-24-7; 2A, 72301-25-8; 2B, 72301-26-9; 3A, 72301-27-0; 3B, 72301-28-1; 4, 2295-12-7; 5, 57787-03-8; (*E*)-1-lithio-1-methoxy-1,3-butadiene, 72301-29-2; chlorodimethylsilane, 1066-35-9; chlorodimethylgermane, 21961-73-9; *trans*-1-methoxy-5,5-dimethylhex-2-ene, 72301-30-5.

Nuclear Magnetic Resonance Configuration Correlation of Primary Amine Derivatives of α-Methyl-α-methoxy(pentafluorophenyl)acetic Acid

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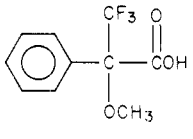
Resolved α-(trifluoromethyl)-α-methoxyphenylacetic acid (MTPA), **1**, and α-methyl-α-methoxy(pentafluorophenyl)acetic acid (MMPA), **2**, have been shown to be



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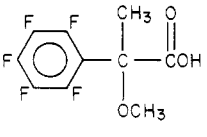

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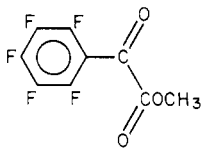

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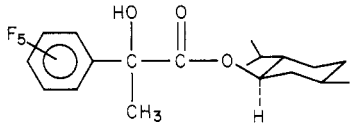
useful reagents for the determination of the enantiomeric composition of secondary alcohols and primary amines.[2-11] For example, the determination of the enantiomeric composition of α- and β-arylethylamine derivatives of **1** and **2** at the subnanogram level has been achieved by utilizing GLC.[9-11] Since many of these substances are biologically active, the technique has considerable utility. Moreover, the technique is not restricted to the determination of enantiomeric purity but can be extended to predict the absolute configuration of the starting alcohol or amine by utilizing ^{1}H NMR. The ^{1}H NMR spectra of the diastereomeric esters and amides derived from **1** and **2** display a pattern of nonequivalence which can be correlated to absolute configuration. An example of the technique used for this purpose can be found in the assignment of absolute configuration to a series of methyl- and methoxyamphetamines of unknown configuration.[9] Since there appears to be a fundamental correlation between configuration and the diastereomeric senses of nonequivalence[12] of the resonances found in the ^{1}H NMR spectra, determination of the factors responsible for the effect and their use in developing a conformational model could be both useful and instructive.

In order to develop such a model, we first found it necessary to assign the absolute configuration of the resolved acid **2**. In our initial approach we attempted to take advantage of Prelog's work[13] and derived relationships[14] in which absolute configuration can be assigned to asymmetric alcohols on the basis of the stereoselective reaction between prochiral precursor α-keto esters and Grignard reagents. Moreover, Hub and Mosher[15] have successfully established the absolute configuration of MTPA by using this same principle. They found that the reaction of phenylmagnesium bromide with (−)-menthyl trifluoropyruvate proceeded with 22% asymmetric induction to yield (−)-α-hydroxy-α-(trifluoromethyl)phenylacetic acid. Accordingly, methyl (pentafluorophenyl)glyoxylate, **3**, was hydrolyzed to the corresponding acid and esterified with (−)-menthol. Reaction of this material with methyl Grignard at 0 °C and lower temperatures gave diastereomeric methyl α-hydroxy-α-methyl(pentafluorophenyl)acetates, **4**, which were present in virtually identical amounts (GLC),



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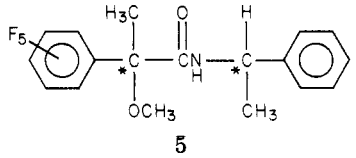

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indicating a lack of asymmetric induction. The lack of induction is surprising, particularly in view of Hub and Mosher's results.[15] One of a number of possible explanations is that the activation of the prochiral keto group by the pentafluorophenyl ring is so intense that product formation results from most collisions. Thus, energy differences in the transition states leading to the two diastereomeric products would be minimized. Other workers have found that asymmetric synthesis based on Prelog's generalization is dependent on subtle interactions between solvents, reagents, and conformational factors.[16]

An attempt to establish the absolute configuration of **2** by relating its circular dichroism (CD) spectrum to existing spectra of α-substituted phenylacetic acids was made.[17] There has been some debate recently concerning

(1) This work was supported in part by NIH Research Career Development Award No. 1 KO4G MUO211 from the Institute of General Medical Science.
(2) J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, **95**, 513 (1973).
(3) G. R. Sullivan, J. A. Dale, and H. S. Mosher, *J. Org. Chem.*, **38**, 2143 (1973).
(4) S. Yamaguchi, F. Yasuhara, and K. Kabuto, *Tetrahedron*, **32**, 1363 (1976).
(5) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **41**, 801 (1976).
(6) H. Hayashi, K. Nakanishi, C. Brandon, and J. Marmur, *J. Am. Chem. Soc.*, **95**, 8749 (1973).
(7) R. C. Cambie, B. R. Davis, R. C. Hayward, and P. D. Woodgate, *Aust. J. Chem.*, **28**, 631 (1975).
(8) K. Mori, *Tetrahedron*, **31**, 3011 (1975).
(9) L. R. Pohl and W. F. Trager, *J. Med. Chem.*, **16**, 475 (1973).
(10) J. Gal, *J. Pharm. Sci.*, **66**, 169 (1977).
(11) D. E. Nichols, C. F. Barfknecht, D. B. Rusterholz, R. Bennington, and R. D. Morin, *J. Med. Chem.*, **16**, 480 (1973).
(12) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **91**, 5150 (1969).
(13) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953); *Bull. Soc. Chim. Fr.*, 987 (1956).
(14) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", 2nd ed., American Chemical Society Books, Washington, DC, 1976.
(15) L. Hub and H. S. Mosher, *J. Org. Chem.*, **35**, 3691 (1970).
(16) S. Yamaguichi, J. A. Dale, and H. S. Mosher, *J. Org. Chem.*, **37**, 3174 (1972).

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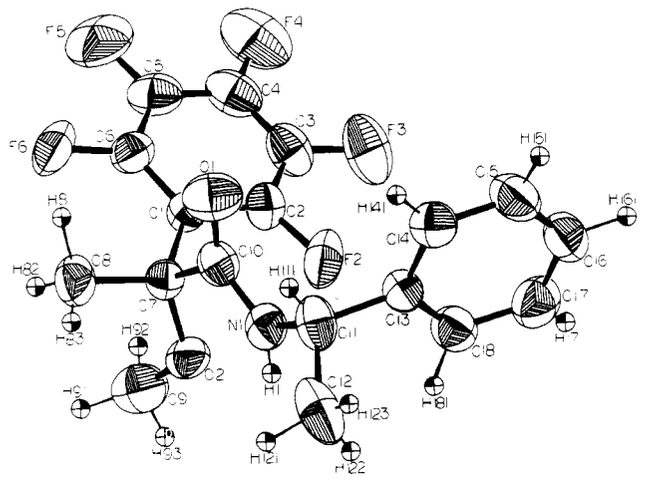

Figure 1. Ellipsoid plot of the structure of *N*-[(*S*)-α-phenylethyl]-(*R*)-α-methyl-α-methoxy(pentafluorophenyl)acetamide (**5**).

the nature of the two Cotton effects (CE) observed in the 220–245-nm region for these compounds, with the weight of experimental evidence favoring a solvent-dependent charge transfer and an n → π* carbonyl transition[18] rather than separate bands arising from different rotamers of a conformationally mobile homoconjugated system.[16,19] Whatever the exact nature of the transition, the more intense shorter wavelength band seems to be related to the configuration of these compounds such that a positive CE correlates with the *S* absolute configuration,[18-23] with some inconsistencies noted. For (+)-**2**, the CD spectrum shows a positive CE (θ +4300) at 218 nm, indicating that it probably has the *S* configuration.

We now report the X-ray crystallographic determination of the absolute configuration of **2** in the form of the crystalline *N*-[(*S*)-α-phenylethyl]-α-methyl-α-methoxy-(pentafluorophenyl)acetamide, **5**, derived from (−)-**2**. The absolute configuration of the (*S*)-(−)-(phenylethyl)amine having already been determined,[24] that of the chiral acid could be unambiguously established.

The crystal structure of **5** is shown in Figure 1. The chain linking the aromatic ends of the molecule has several interesting features (Figure 2). The amide group is nearly planar, as anticipated, with the amide hydrogen linking N(1) to the methoxyl oxygen, O(2), through a hydrogen bond [N(1)–O(2) = 2.57 Å]. The pentafluorophenyl and methyl groups of the mandelic acid moiety are disposed on opposite sides of the amide group. In the (arylethyl)-amino moiety, the methine hydrogen is rotated 29° away from the plane described by the amide group, adopting an arrangement roughly cis to the carbonyl group. Such an orientation is thought to be a relatively stable one, possibly involving a very weak interaction between O(1) and H-(111).[25] The phenyl and pentafluorophenyl are on the same side of the amide group in a staggered arrangement such that the planes of the two rings are approximately perpendicular to each other. There are no intermolecular

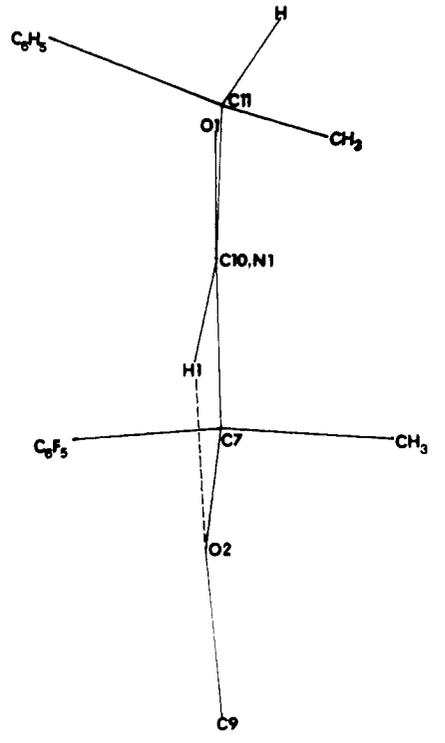

Figure 2. Skeleton drawing of **5**, showing the disposition of the substituents with respect to the amide plane.

contacts less than 3.0 Å. The relative configurations at the asymmetric centers, C(7) and C(11), are opposite, and the absolute configuration of (−)-**2** is confirmed as *R*, since the amine moiety has the *S* configuration. This result is in agreement with that suggested by the CD spectrum of the resolved acid.

The intramolecular interactions exhibited by **5** in the crystal are of a nature that could significantly affect its predominant solution conformation. The arrangement of the carbinyl hydrogen roughly cis to the carbonyl group has been shown to be a relatively favored conformation over other possible rotamers,[5,26] both in solution and in the solid state in similar systems. The NH···OCH_3 hydrogen bond should likewise make a strong contribution to the molecular conformation at the acid end of the molecule. Hence we assume that the solid-state conformation is a major contributor to the preferred conformation in solution. Since no apparent destabilizing factors are introduced by conversion to the other diastereomer, on the basis of molecular models, a similar conformation should also be the preferred conformation for this substance. In these conformations the substituents on the asymmetric carbon atoms may be viewed (end-on) as approximately staggered. In addition, the conformational model proposed herein is identical with that advanced by Helmchen et al.[27] to rationalize the sense of nonequivalence between the diastereomeric phenylethyl amides of *o*-methylmandelic acid.

In the ^1H NMR spectrum of the diastereomeric (pentafluorophenyl)acetamides one would expect that the chemical shifts of groups oriented cis with respect to either the phenyl or the pentafluorophenyl rings would be affected by the ring currents of these groups to a greater extent than they would be when oriented trans to such groups. The effect could be either shielding or "deshielding" depending on the specific time-averaged

(17) G. Barth, W. Voelter, H. S. Mosher, E. Bunnenberg, and C. Djerassi, *J. Am. Chem. Soc.*, **92**, 875 (1970).
(18) T. Polonski, *Tetrahedron*, **31**, 347 (1975).
(19) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).
(20) S. Rendic, V. Sankic, F. Kajfez, N. Bluzevic, and T. Alebic-Kolbah, *Chimica*, **29**, 197 (1975).
(21) O. Korver, *Tetrahedron*, **26**, 5507 (1970).
(22) W. Gaffield and W. G. Galetto, *Tetrahedron*, **27**, 915 (1971).
(23) H. Meguro, H. Hachiya, K. Tuzimura, K. Mori, and M. Matsui, *Agric. Biol. Chem.*, **37**(5), 1035 (1973).
(24) W. Leithe, *Ber. Dtsch. Chem. Ges.*, **64**, 1817 (1931).
(25) A. M. Mathieson, *Tetrahedron Lett.*, 4137 (1965).
(26) C. C. J. Culvenor, *Tetrahedron Lett.*, 1091 (1966).
(27) G. Helmchen, R. Ott, and K. Sanber, *Tetrahedron Lett.*, 3873 (1972).

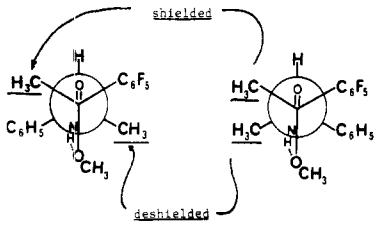

Figure 3. Relative shielding/deshielding model for α-arylethyl amide derivatives of MMPA, shown for **5**.

orientation of the aromatic system with respect to these groups. If the solid-state conformation of the phenyl and pentafluorophenyl groups with respect to the methoxyl carbon–amide–carbinyl carbon plane is retained in solution, then the benzylic methyl group (acid moiety) should be shifted upfield in the diastereomer where it is oriented cis with respect to the phenyl group relative to the diastereomer where it is oriented trans with respect to the phenyl group. A similar effect should be exerted on the carbinyl methyl group (amine moiety) by the pentafluorophenyl ring. However, insofar as it adopts the conformation seen in the solid state, Figure 1, the expected shielding effect of the cis conformation could be reduced or even reversed relative to the observed effect for the phenyl ring. The latter effect is what is seen experimentally.[9] That is, the pentafluorophenyl group deshields the carbinyl methyl group when it is oriented cis with respect to it while the phenyl group shields the benzylic methyl group when it is oriented cis with respect to it. The net effect is that in amides with the *R,S* or *S,R* configuration the carbinyl methyl is shifted upfield while the benzylic methyl is shifted downfield relative to their positions in amides having the *R,R* or *S,S* configuration (Figure 3). Since the configuration correlation is based on ^{1}H NMR effects due to minimum-energy conformations, deviations or exceptions to the predicted pattern should be readily apparent in terms of structural features which compete with or disrupt the stabilizing influences of the intramolecular hydrogen bond and *cisoid* carbonyl–carbinyl hydrogen conformation. Hence, use of MMPA should provide strong evidence for the assignment of absolute configuration to substituted α-arylethylamines. Moreover, the same shielding/deshielding pattern is maintained in β-arylethylamine,[9] and an examination of Dreiding models reveal that a similar conformational preference should prevail.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer, and chemical shifts are reported in ppm (δ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr disks. Circular dichroism spectra were measured on a JASCO ORD/CD spectrophotometer.

(Pentafluorophenyl)glyoxylic Acid. Methyl (pentafluorophenyl)glyoxylate[9] (3.0 g, 0.012 mol) was hydrolyzed in a mixture of 44 mL of dioxane distilled from calcium hydride, 44 mL of water, and 20 mL of concentrated HCl for 7.5 h at 80 °C. The reaction solution was vacuum evaporated and the residual oil recrystallized from benzene, giving 1.3 g (46%) of product as plate crystals: mp 71–74 °C; IR 3600–3100 (br), 1720, 1645, 1490, 1405, 1320, 1150, 990 cm^{-1}.

Menthyl (Pentafluorophenyl)glyoxylate. McKenzie's procedure[28] for the synthesis of menthyl phenylglyoxylate was followed for the preparation of the title compound. A mixture of (pentafluorophenyl)glyoxylate (0.9 g, 0.0038 mol) and (−)-menthol (2.7 g, 0.0173 mol) gave 1.3 g (90%) of the product as an oil: IR (neat) 2960, 2940, 2870, 1775 (sh), 1745, 1665, 1540, 1520, 1475, 1290, 1000, 950, 800 cm^{-1}.

Menthyl α-Hydroxy-α-methyl(pentafluorophenyl)acetate (4). An ethereal solution, 25 mL, of methylmagnesium iodide generated from 0.57 g of methyl iodide (0.004 mol) was added dropwise to a 20-mL ice-cold ether solution of methyl (pentafluorophenyl)glyoxylate (1.3 g, 0.0038 mol). The solution was stirred at 0 °C for 1.5 h and then refluxed for an additional 0.5 h. The reaction was terminated by the addition of 20 mL of 1 N HCl. The ether layer was separated, washed with water, and dried over magnesium sulfate. A mixture of the diastereoisomers of 4 was obtained as an oil (1.3 g, 90%) upon vacuum evaporation of the dried ether solution: IR (neat) 3480, 2950, 2935, 2860, 1750, 1660, 1540, 1510, 1475, 1255, 1140, 990, 850, 715 cm^{-1}. Separation by GC (3% OV-17, 3 mm × 6 ft, 155 °C, He 20 mL/min) gave two peaks of equal integrated area at 16 and 19 min, indicating the absence of asymmetric induction. Repetition of the reaction at −10 °C (methanol–ice) and −77 °C (dry ice–acetone) with methylmagnesium iodide or at −10 °C with methylmagnesium bromide gave similar results.

(+)-α-Methyl-α-methoxy(pentafluorophenyl)acetic Acid (2). Resolved **2** was obtained as previously reported.[9] The circular dichroism spectrum was determined in 95% ethanol: concentration 0.002 42 g/mL, 1-mm path length, 28–29 °C, molecular elipticity [θ] 218 nm +4300, 240 (crossover), 260, −213.

X-Ray Crystallographic Measurements. Crystals of *N*-[(*S*)-α-phenylethyl]-(−)-α-methyl-α-methoxy(pentafluorophenyl)acetamide[9] (**5**) formed as plates from hexane–benzene. A specimen of 0.4 × 0.6 × 0.15 mm was chosen for the X-ray work. Preliminary photographs revealed the space group $P2_12_12_1$ ($h00$ absent for $h = 2n + 1$, $0k0$ absent for $k = 2n + 1$, $00l$ absent for $l = 2n + 1$). Cell constants were determined by centering 12 reflections on a computer-controlled four-circle diffractometer and found to be a = 11.395 (2) Å, b = 8.815 (1) Å, and c = 17.561 (3) Å (estimated standard deviations in parentheses). The crystal density, determined by suspension in KI density-gradient solutions, was observed to be 1.42 (1) g/cm^3 compared to the 1.415-g/cm^3 calculated value. A total of 1792 Friedel-related pairs of reflections were collected by using Mo Kα (λ = 0.710 69 Å) radiation and a Nb filter. Background counts which were measured at each limit of the 1° scan range increased proportionately for the α_1–α_2 separation. Five monitor reflections were observed periodically during the collection of data, and no trend attributable to deterioration of the crystal was detected. The raw data were reduced, and coincidence, absorption, Lorentz, and polarization corrections were applied; the Friedel pairs of reflections were not averaged but treated as unique measurements. The data were converted to E values, those 297 reflections with $E > 1.5$ were supplied to program MULTAN,[29] and a starting set of phases was generated. An E map computed from this set revealed the mandelic acid portion of the molecule, two additional Fourier maps being necessary to locate all the nonhydrogen atoms. In the early stages of refinement, only the positive Friedel reflections were used. Two cycles of least-squares refinement on all of the nonhydrogen atoms and their isotropic parameters (vibrational amplitudes) lowered R to 0.14. One cycle of least-squares refinement on the positional and anisotropic parameters (U's) for the nonhydrogen atoms further reduced R to 0.084. A difference Fourier map computed at this point revealed the position of all 16 hydrogen atoms. The hydrogen atoms were assigned B's of 6.0 Å^2 and refined with their positional parameters with the nonhydrogen atoms half-fixed, reducing R in one cycle to 0.072. At this point, all reflections were included with unit weights, and all positional parameters, the U's for the nonhydrogen atoms, and the B's for the hydrogen atoms were refined for three cycles, lowering R to 0.041. The shifts in all parameters were less than one standard deviation during the final cycle of refinement. Programs used in the refinement were part of the XRAY system[30] of routines. A drawing of the structure is given in Figure 1.

(28) A. McKenzie, *J. Chem. Soc.*, 85, 1249 (1964).

(29) P. Main, M. M. Woolfson, and G. Germain, "MULTAN, A Computer Program for the Automatic Solution of Crystal Structures", University of York Printing Unit, York, England, 1971.

(30) J. M. Stewart, F. A. Kundell, and T. C. Baldwin, "X-RAY System", University of Maryland, College Park, MD, 1970.

Acknowledgment. We are grateful to Dr. Lyle H. Jensen of the Department of Biological Structure, University of Washington, for helpful discussions and use of the diffraction equipment. We are also grateful to L. Sicker and Dr. K. Watenpaugh for technical assistance.

Registry No. (-)-**2**, 50502-38-0; **3**, 38449-80-8; **4**, isomer 1, 72331-52-3; **4**, isomer 2, 72331-53-4; **5**, 72376-91-1; (pentafluorophenyl)glyoxylic acid, 72331-54-5; menthyl (pentafluorophenyl)glyoxylate, 72331-55-6.

Supplementary Material Available: Atom positional parameters, bond lengths, and angles for compound **5** (3 pages). Ordering information is given on any current masthead page.

Intramolecular Nucleophilic Participation. 12. Solvolysis of *o*-(Carbophenoxy)benzhydryl Bromide in 2,2,2-Trifluoroethanol–Benzene Mixtures

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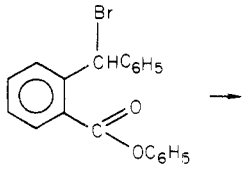
Evidence has been presented in earlier publications[1] that the solvolysis of *o*-(carbophenoxy)benzhydryl bromide (**1**)



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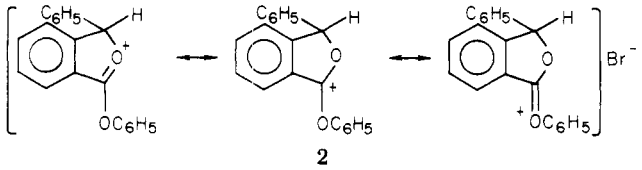

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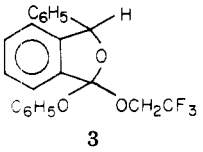
in nucleophilic media is subject to anchimeric assistance by the carbophenoxy group. The reaction is presumed to proceed by way of a cationic (or ion pair) intermediate (**2**) in which a nonbonding electron pair of the carbonyl oxygen of the ortho substituent is shared with carbon at the reaction center. The product isolated from the reaction in aqueous acetone or in acetic acid is 3-phenylphthalide.

Recent studies of the products and kinetics of the reaction of **1** in 2,2,2-trifluoroethanol (TFE)–benzene mixtures in the presence of 2,6-lutidine have provided further evidence of the involvement of the carbophenoxy group as an internal nucleophile in the solvolytic process. At room temperature the immediate product of reaction in TFE–benzene is the ortho ester **3**. The yield of the



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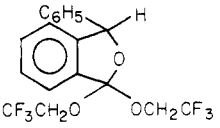
product **3** is by no means quantitative since it is converted relatively rapidly in the medium to the ortho ester **4**, very



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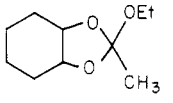
likely by a process involving acid catalysis by lutidinium ion or trifluoroethanol. Compound **4** has been recovered only in small quantity and not in highly pure form, since apparently it decomposes readily to form 3-phenylphthalide. The trapping of the cationic intermediate **2** by solvent with the production of ortho ester calls to mind the experiments of Winstein and Buckles,[2] who isolated the ortho ester **5** (cis isomer) as the product of ethanolysis



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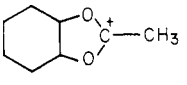
of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate in absolute ethanol under acid-free conditions. The recovery of **5** as the solvolysis product strongly supported the view that the cation **6** (cis) is formed as a solvolysis intermediate through participation of the acetoxy group as a nucleophile.



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Because of the high reactivity of **1** in TFE–benzene mixtures it has not proved feasible to carry out an extensive investigation of the kinetics of its solvolysis. The results of the limited number of rate measurements which have been made do, however, suggest that the *o*-carbophenoxy group provides extensive anchimeric assistance, considerably more than occurs during hydrolysis[1a] and acetolysis[1b] of **1**. As in earlier work[1b] the solvolysis rate of **1** has been compared with the solvolysis rates of *p*-(carbophenoxy)benzhydryl bromide and the *o*- and *p*-bromobenzhydryl bromides. The k_{ortho}/k_{para} rate ratios for reaction of the bromobenzhydryl bromides in TFE–benzene at 10.6 °C in the presence of 2,6-lutidine are 0.091 (20% TFE) and 0.099 (40% TFE); that is, the ortho isomer is less reactive than the para when the ortho substituent, in this case Br, is nonparticipating. The corresponding rate constant ratios, k_{ortho}/k_{para}, for the (carbophenoxy)-benzhydryl bromides at 10.6 °C are approximately 3200 (20% TFE) and 3100 (40% TFE).

The very high rate constant ratios, k_{ortho}/k_{para}, for the carbophenoxy compounds in TFE–benzene are supportive of the generally accepted belief that anchimeric assistance by an internal nucleophile (in this case *o*-$COOC_6H_5$) should be increasingly reflected in the solvolysis rate as the medium nucleophilicity decreases (trifluoroethanol is considered to be closely comparable in nucleophilicity to formic acid).[3] The possibility cannot be excluded, however, that the solvolysis of the para isomer is more subject to return than is that of the ortho isomer. If this is the case, k_{ortho}/k_{para} ratios are correspondingly inflated, and the extent of anchimeric assistance by the ortho substituent, as measured by those ratios, is overstated.[4]

(1) (a) A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962); (b) S. Kim, S. S. Friedrich, L. J. Andrews, and R. M. Keefer, *ibid.*, **92**, 5452 (1970); (c) E. A. Jeffery, R. K. Bansal, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **29**, 3365 (1964).

(2) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **65**, 613 (1943).

(3) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970); (b) M. D. Bentley and J. A. Lacadie, *Tetrahedron Lett.*, 741 (1971).

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