Table I. Single-Crystal X-ray Crystallographic Analysis

A. Crystal Parameters	
formula	$C_{18}H_{30}NO_4$ (324.4)
crystallization medium	hexane/dichloromethane
crystal size, mm	0.06 × 0.09 × 0.09
cell dimensions	
a, Å	11.2775 (8)
b, Å	11.2775 (8)
c, Å	27.646 (3)
α, deg	90.0
β, deg	90.0
γ, deg	120.0
ν, Å^3	3045 (1)
space group	$P6_1$
molecules/unit cell	6
density	
obsd, g/cm^3	1.03
calcd, g/cm^3	1.06
linear absorption coefficient, cm^{-1}	5.66
B. Refinement Parameters	
number of reflections	2033
nonzero reflections ($1 > 3.0\sigma$)	1435
R index = $\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	.080
GOF = $[\sum w(F_o^2 - F_c^2)^2/(m-s)]^{1/2}$	1.40
scale factor	1.266 (5)
secondary extinction coefficient	12 (5) × 10^{-4}

The refined structure was plotted using the SHELXTL plotting package (Figure 2). Coordinates, anisotropic temperature factors, distances and angles are available as supplementary material (Tables S1-S5).

The fractions containing the more polar cis lactone **11** (R_f 0.44 1:1 ether-hexane) were combined and evaporated to 39 mg (3%) of a white solid: mp 96-98 °C; ^{1}H NMR (250 MHz) δ 0.92 (6 H, d, J = 6), 1.43 (9 H, s), 1.72 (3 H, s), 2.02-2.14 (1 H, m) 2.23-2.36 (1 H, m), 2.60-2.87 (2 H, m), 3.74-3.89 (1 H, m), 4.35-4.47 (2 H, m), 4.69 (1 H, s), 4.78 (1 H, s); ^{13}C NMR (75 MHz) δ 21.9, 22.0, 23.0, 24.8, 28.3, 30.7, 38.8, 38.9, 42.3, 50.1, 79.6, 80.4, 112.6, 142.0, 155.9, 178.7; IR ($CHCl_3$) 3443, 1774, 1714, 1656 cm^{-1}; $[\alpha]_D$ -0.6° (c 0.5, CH_3OH).

Anal. Calcd for $C_{18}H_{31}NO_4$; C, 66.43; H, 9.60; N, 4.30. Found: C, 66.94; H, 9.45; N, 4.27.

(3*R*,5*S*)-5-((1*S*)-1-(*N*-Boc-amino)-3-methylbutyl)-3-(2-methylpropyl)dihydrofuran-2(3*H*)-one (1). An ethyl acetate (10 mL) solution of 438 mg (1.35 mmol) of lactone **10** containing 44 mg of 10% Pd/C was hydrogenated on a Parr Shaker apparatus at 50 psi for 2 h. After filtration of the catalyst and evaporation of the solvent, 437 mg (99%) of lactone **1** was obtained as a white solid: mp 130-131 °C; ^{1}H NMR (300 MHz) δ 0.84-0.97 (12 H, m), 1.41 (9 H, s) 1.86-1.96 (1 H, m), 2.30-2.42 (1 H, m), 2.56-2.68 (1 H, m), 3.76-3.89 (1 H, m), 4.35 (1 H, d, J = 8), 4.45 (1 H, br t); ^{13}C NMR (75 Hz) δ 21.3, 21.8, 22.9, 23.0, 24.8, 26.1, 28.3, 31.0, 37.7, 40.5, 41.9, 51.7, 79.8, 80.5, 156.0, 180.3; IR ($CHCl_3$) 3439, 1769, 1713 cm^{-1}, [α] -32.1° (c 1.0, CH_3OH).

Anal. Calcd for $C_{18}H_{33}NO_4$: C, 66.02; H, 10.16; N, 4.28. Found: C, 66.07; H, 10.03; N, 4.05.

Acknowledgment. We gratefully acknowledge Dr. Jon Bordner for obtaining the single-crystal X-ray structure of lactone **10**. We thank Professors E. J. Corey, D. S. Kemp, and S. L. Schreiber and Drs. J. S. Bindra, D. J. Hoover, and R. L. Rosati for helpful discussions. We also thank Gary E. Berg for technical assistance.

Registry No. **1**, 105018-80-2; **2**, 105018-81-3; **3**, 58521-45-2; (4*S*,5*S*)-**4**, 105018-82-4; (4*R*,5*S*)-**4**, 105018-89-1; **5**, 105018-83-5; **6**, 67010-44-0; **7**, 105018-84-6; **8**, 105018-85-7; **9**, 105018-86-8; **10**, 105018-87-9; **11**, 105018-88-0; *N*-Boc-L-leucine methyl ester, 63096-02-6; ethyl propiolate, 623-47-2; α-lithio ethyl acetate, 26954-26-7; 2-methoxypropene, 116-11-0; methallyl bromide, 1458-98-6.

Supplementary Material Available: Crystallographic data including tables of the atomic positional and thermal parameters and bond angles for **10** (4 pages). Ordering information is given on any current masthead page.

Iodination of Aryltrimethylsilanes: A Mild Approach to Iodophenylalanine

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Phenylalanine has been labeled with the radioactive isotopes of iodine by using harsh conditions or toxic mercury compounds. A mild method of incorporating iodine onto an aryl ring was developed that combines two methods that have been used separately for the production of aryl iodides: (1) the use of a Lewis acid to activate the electrophile, I_2, and (2) the use of a trimethylsilyl group to direct the introduction of iodine. Simple aryltrimethylsilanes and a phenylalanine-containing peptide were successfully iodinated by this method.

The use of iodine-125-containing compounds for metabolic and radiolabeling studies is widespread.[1] The various iodophenylalanine isomers have been used for pancreatic imaging studies,[2] and other radioiodinated drugs have been studied to ascertain their accumulation in the various parts of the body.[3] The thyroid hormones, amphetamines, and the numerous corticosteroids have been investigated by using radioiodine derivatives.[1]

The methods for introducing iodine onto a phenyl ring are numerous and vary greatly.[1,2,4-8,13] Most of them re-

(1) Colombetti, L. G. *Principles of Radiopharmacology*; CRC Press: Boca Raton, 1979; Vol. 1, pp 189-250 and references therein.
(2) Counsell, R. E.; Smith, T. D.; Diguilo, W.; Beierwaltes, W. H. *J. Pharm. Sci.* **1968**, *57*, 1958.
(3) Korn, N.; Buswimk, A.; Yu, T.; Carr, E. A., Jr.; Carroll, M.; Counsell, R. E. *J. Nucl. Med.* **1977**, *18*, 87.
(4) (a) Fleming, I. In *Comprehensive Organic Chemistry*; Vol. 3, Barton, D., Ollis, W. D., Eds.; Pergamon Press, Oxford: 1979; Vol. 3, pp 541-686. (b) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43-57.
(5) Eaborn, C.; Najam, A. A.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2481.

0022-3263/86/1951-4833$01.50/0

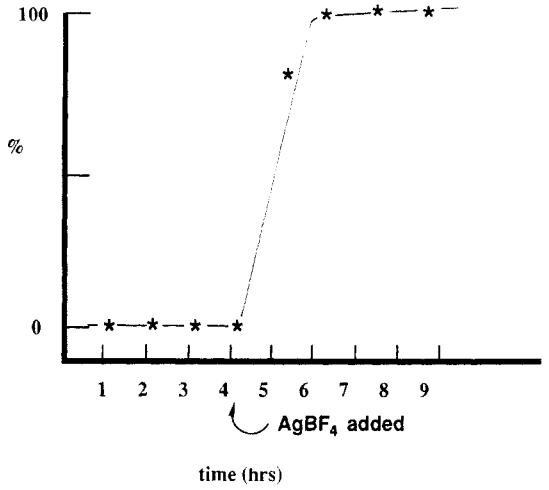
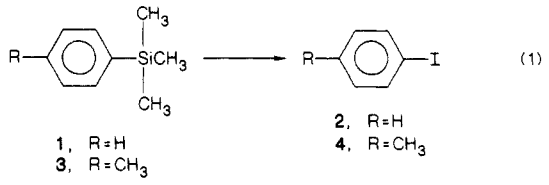


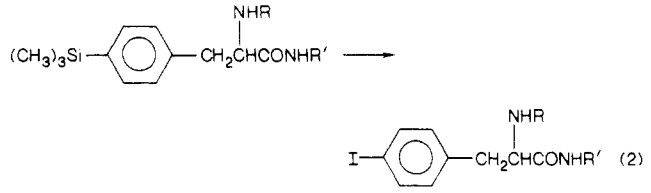
Figure 1.

quire an activated ring, such as tyrosine, the use of toxic mercury or thallium salts, or harsh conditions.

We would like to present a method of directly introducing iodine onto a phenyl ring (eq 1). Our approach



combines two methods that have been used separately for the production of aryl iodides: (1) the use of the trimethylsilyl group to direct the introduction of iodine and (2) a Lewis acid to activate the electrophile, I_2. Eventually, it is our intention to use this method to incorporate iodine into an intact phenylalanine-containing peptide with easily removed protecting groups. This method is mild and yields a product that is easy to purify (eq 2).



Eaborn[4] and others[13] have studied the substitution of the trimethylsilyl group extensively. Electrophiles attack the silicon-bearing carbon, because the cationic intermediate is stabilized by the neighboring carbon–silicon bond (eq 3). The $(CH_3)_3Si$ group is thus more readily replaced

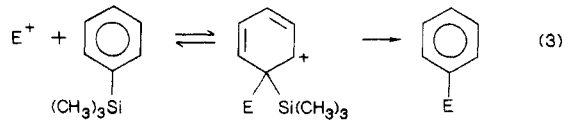


Table I. Reaction of (Trimethylsilyl)benzene 1 with I_2/AgX

silver salt	equiv	temp, °C	time, h	yield,[a] %
$AgNO_3$	1.1	23	1	57 (>95)
AgOBz[b]	1.1	68	16	(50)
AgOAc[b]	1.1	68	16	(0)
$AgBF_4$	1.1	0	1/2	59 (>95)
CF_3CO_2Ag	1.0	0–23	3–4	(0)
	1.5	0	1	(50)
	2.1	0	1	56 (>95)

[a] Yields reported are for isolated yields. Yields in parentheses are GC yields. [b] Silver salt not completely soluble in methanol.

Table II. Iodination of Substituted Aryl Compounds

	silver salt	time	yield,[a] %
3	$AgBF_4$	15 min	60 (>95)
	$AgCF_3CO_2$	15 min	65 (>95)
5	$AgBF_4$	1 h	65 (>95)
	$AgCF_3CO_2$	1 h	73 (>95)
7	$AgBF_4$	15 min	86 (>95)
9	$AgBF_4$	30 min	54
11	$AgCF_3CO_2$	15 min	0

[a] Yields reported are for isolated yields. Yields in parentheses are GC yields.

by electrophiles and directs the regioselective introduction of iodine.

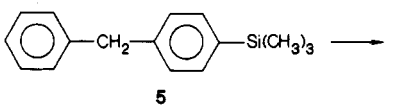
Silver salts have been used as Lewis acid catalysts for the introduction of iodine onto phenyl rings[7,14] and have several advantages. After the heterolytic cleavage of the iodine, precipitation of AgI removes the residual iodide ions from the reaction very rapidly. This prevents the interference of the iodide with other functional groups. In the absence of a silver salt, unactivated arene rings, such as present in **1–3** fail to react with iodine. This is shown by the graph in Figure 1. Phenyltrimethylsilane (**1**) was treated with iodine in methanol at ambient temperature. No conversion of **1** into **2** was observed for 4 h. At this time (t), 1.1 equiv of $AgBF_4$ were added. The iodination started immediately and was complete within an hour. The reaction was monitored by GC for several hours after completion. The formation of **2** was the only reaction observed.

Several silver salts were investigated as catalysts for the transformation in eq 1. It was found that the silver salt must be soluble in the desired solvent, the best combination being methanol and $AgBF_4$. To avoid the formation of side products when using $AgBF_4$ and $AgNO_3$, great care must be exercised in the drying of the methanol. Two equivalents of CF_3CO_2Ag and iodine were required for the reaction to go to completion. These results are collected in Table I.

The studies on **1** were followed by the investigation of substituted silanes **3** and **5**. Regiospecific competition between the substitution of the trimethylsilyl group or a proton can be seen by using **5** (eq 4). Proton substitution (i.e., *p*-iodo-*p'*-(trimethylsilyl)diphenylsilane or *p,p'*-diiododiphenylmethane) product was not observed by GC or NMR. Under the conditions mentioned above, both **3** and **5** reacted cleanly to give only the desired iododinated product (Table II).

The next step was to test this procedure on compounds with more sensitive functionality. An amino acid deriva-

(6) Pray, B. D.; Sommer, L. H.; Goldberg, G. M.; Kerr, P. A.; DiGiogio, P. A.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 433.
(7) Janssen, D. E.; Wilson, C. V. *Organic Synthesis*; Wiley: New York, 1963, Collect. Vol. IV, p 547.
(8) Visser, G. W. M.; Diemer, E. L.; Kaspersen, F. M. *J. Labelled Compd. Radiopharm.* **1980**, *17*, 657–665.
(9) Eaborn, C.; Lasocki, Z.; Sperry, J. A. *J. Organomet. Chem.* **1972**, *35*, 245–252.
(10) Frankel, M.; Gertner, D.; Shenar, A.; Zilkha, A. *J. Chem. Soc.* **1963**, 5049–5051.
(11) Frankel, M.; Gertner, D.; Shenar, A.; Zilkha, A. *J. Chem. Soc.* **1967**, 1334–1336.
(12) Rundle, R. E.; Goring, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 5337.
(13) Felix, G.; Dunogues, J.; Pisciotti, F.; Calas, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 488.
(14) The reacive species may be an acyl hypoiodite[15] or hypoiodous acid ester,[16] which have been shown to iodinate aryl rings[15] and double bonds.[15,16]
(15) (a) Bergmann, E. D.; Shahak, I. *J. Chem. Soc.* **1959**, 1418–1422. (b) Henne, A. L.; Zimmer, W. F. *J. Am. Chem. Soc.* **1951**, *73*, 1362–1363. (c) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. *Synthesis* **1980**, 486–487.
(16) Glover, S. A.; Goosen, A. *Tetrahedron Lett.* **1980**, *21*, 2005–2008.



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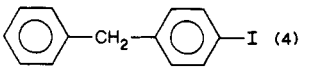
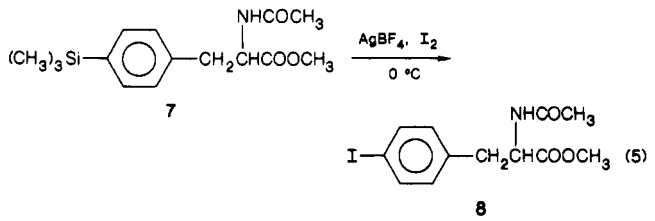


6

tive (7), a dipeptide (9), and a pencillin derivative (11) were chosen, since these molecules contain more than one functional group and are of biological significance. Previously, iodophenylalanine derivatives were made from the malonate precursors.[2,8a] If the radiolabeled adduct was desired, this was made by exchange with an inorganic iodide or the appropriate mercury derivative.[8]

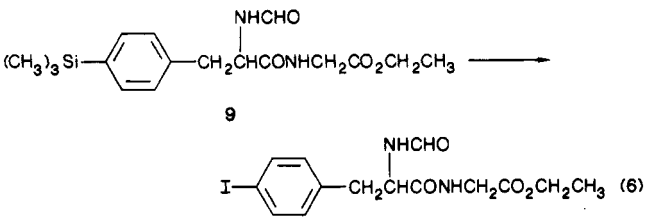
The reaction of the phenylalanine derivative 7 proceeded rapidly and cleanly (eq 5). The necessity of having the



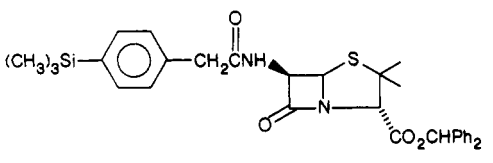
7 8

trimethylsilyl group on the phenyl ring was demonstrated by the failure of *N*-acetylphenylalanine methyl ester to react under the same conditions used to iodinate 7, even when extended reaction times were used. The amide and ester linkages remained untouched, presenting the possibility of using this reaction on small peptides, which do not contain tyrosine or some other readily iodinated function.

The utility of this reaction was tested further with the dipeptide 9 (eq 6). This contains the more readily re-



9 10



11

movable formamido protecting group on the amine function and an ethyl ester. An extremely clean product was obtained from the iodination. No transesterification or loss of the formamido group was observed in the NMR of the product obtained. Unfortunately, the penicillin derivative 11 was decomposed by these reaction conditions, probably due to the attack of the silver salt or iodine on the sulfur or β-lactam ring.

Table II shows the results of the substituted aryl compounds. All reactions were run at 0 °C in dry methanol using 2.2 equiv of CF_3CO_2Ag and 2.0 equiv of I_2 or 1.1 equiv of $AgBF_4$ and 1.0 equiv of I_2.

This reaction presents a mild method of incorporating iodine onto an unactivated phenyl ring. A variety of functional groups can be tolerated. Thus, the very stable $(CH_3)_3Si$ substituent might be used as a masked iodine precurser for the synthesis of affinity ligands or other labeled precursers, where the radioactive ^{125}I is inserted as the final step in the synthesis.

Experimental Section

NMR spectra were taken on a General Electric QE 300 spectrometer. GC/MS spectra were taken on a Hewlett-Packard 5992 GC/MS system. Melting points are uncorrected and taken with a Thomas-Hoover capillary melting point apparatus.

General Procedure. All methanol used in these experiments was dried by refluxing it with magnesium turnings and a few drops of carbon tetrachloride and distilled just prior to use.

Iodobenzene (2). Phenyltrimethylsilane (1) (0.30 g, 2.0 mmol) was dissolved with stirring in methanol (10 mL) under nitrogen. This was cooled in an ice bath to 0 °C. Silver trifluoroacetate (0.93 g, 4.2 mmol) was added and stirred for 5 min to ensure complete dissolution. The iodine (1.2 g, 4.0 mmol) was added and the mixture stirred at 0 °C for 1 h. Gas chromatographic analysis of the reaction mixture showed complete absence of the starting material and no formation of any multiiodo products. The product was recovered by diluting with ether (20 mL), filtering through Celite and washing the cake with ether. The filtrates were washed twice with 10% sodium thiosulfate (10 mL), dried over magnesium sulfate, and concentrated under reduced pressure to yield 0.23 g (56%) of 2 and was pure by GC: NMR ($CDCl_3$) 7.14 (t, 2 H, J = 7 Hz), 7.36 (t, 1 H, J = 7 Hz), 7.74 (d, 2 H, J = 3 Hz); MS, m/e (relative intensity) M = 204 (100), M + 1 = 205 (6.9).

Due to the volatility of the product an increase in yield is observed, if the scale of the reaction is increased. When 1 g (6.7 mmol) of 1 was used, the recovered yield was 75%. Since radioactive labeling is usually carried out on a small scale, it was felt that the lower yield was a more realistic result.

4-Iodotoluene (4). 4-(Trimethylsilyl)toluene (3) was prepared as previously reported.[10] 1 (0.41 g, 2.5 mmol) was dissolved in dry methanol (8 mL) under N_2. Silver trifluoroacetate (1.11 g, 5.0 mmol) was added with stirring and permitted to dissolve completely. The reaction was cooled to 0 °C. The iodine (1.27 g, 5.0 mmol) was added all at once. Within 15 min the reaction was complete by GC analysis. The reaction was diluted with ether (30 mL), filtered through Celite, and washed twice with 10% sodium thiosulfate, and the ether layers were dried with $MgSO_4$. After removing the solvent, the yield was 0.35 g (64.8%) of 4 and was pure by GC: NMR ($CDCl_3$) 2.29 (s, 3 H), 6.92 (s, 2 H, J = 4 Hz), 7.56 (d, 2 H, J = 4 Hz); MS, m/e (relative intensity) M = 218 (100), M + 1 = 219 (7.3).

4-Iododiphenylmethane (6). 4-(Trimethylsilyl)diphenylmethane (5) was prepared as previously reported.[9] 5 (177 mg, 0.74 mmol) was reacted as above with silver tetrafluoroborate (160 mg, 0.82 mmol) and iodine (190 mg, 0.75 mmol) in dry methanol. The yield was 141 mg of 5 (65%) and the product was pure by GC: NMR ($CDCl_3$) 3.98 (s, 2 H), 6.99 (d, 2 H, 8 Hz), 7.30 (d, 2 H, 8 Hz); MS m/e (relative intensity) M = 294 (100), M + 1 = 295 (15).

***N*-Acetyl-4-iodophenylalanine Methyl Ester (8).** *N*-Acetyl-4-phenylalanine (7) was prepared as previously reported.[10] 7 (40.0 mg, 0.14 mmol) was dissolved in 5 mL of dry methanol under nitrogen. Silver tetrafluoroborate (32 mg, 0.16 mmol) was added and allowed to dissolve. The solution was cooled to 0 °C. The iodine (36 mg, 0.14 mmol) was dissolved in 1 mL of dry methanol and added dropwise. GC analysis indicated that the reaction was not complete for 1 h. After stirring the mixture at 0 °C for 1 h, the reaction was worked up as usual. The yield of 8 was 40.5 mg of a white solid (mp 122–124 °C) (85.6%), pure by GC: NMR ($CDCl_3$) 2.00 (s, 3 H), 3.07 (s, 3 H), 3.74 (s, 3 h), 4.86 (m, 1 H), 5.80 (d, 1 H, J = 6 Hz), 6.34 (d, 2 H, J = 8 hz), 7.61 (d, 2 H, J = 8 Hz). Anal. Calcd for $C_{12}H_{14}INO_3$: C, 41.52, H, 4.07, N, 4.04. Found: C, 41.44, H, 3.97, N, 3.97.

***N*-Formyl-4-iodophenylalanylglycine Ethyl Ester (10).** *N*-Formyl-4-(trimethylsilyl)phenylalanylglycine ethyl ester (9) was prepared as previously reported.[11] 9 (175 mg, 0.50 mmol) was reacted as above with silver tetrafluoroborate (107 mg, 0.55 mmol) in dry methanol (10 mL) and iodine (127 mg, 0.50 mmol) in dry methanol (2 mL). The yield of 10 was 110 mg of a white solid (mp 160–161 °C) (54.5%), pure by NMR: NMR ($CDCL_3$

+ 3 drops Me_2SO-d_6) 1.15 (t, 3 H), 2.92 (m, 2 H), 3,83 (t, 2 H), 4.06 (q, 2 H), 4.73 (q, 1 H), 6.88 (d, 2 H), 7.32 (d, 1 H), 7.46 (d, 2 H), 7.53 (m, 1 H), 7.98 (s, 1 H). Anal. Calcd for $C_{17}H_{17}IN_2O_4$: C, 41.60, H, 4.24, N, 6.93. Found: C, 41.40, H, 4.10, N, 6.61.

Registry No. 1, 768-32-1; 2, 591-50-4; 3, 3728-43-6; 4, 624-31-7; 5, 17964-29-3; 6, 35444-94-1; 7, 105089-60-9; 8, 105089-61-0; 9, 105120-26-1; 10, 105089-62-1; 11, 105089-63-2; $AgNO_3$, 7761-88-8; AgOBz, 532-31-0; $AgBF_4$, 14104-20-2; CF_3CO_2Ag, 2966-50-9.

Resolution and Assignment of Absolute Configuration to the Enantiomers of Anastrephin and Epianastrephin and Their Analogues

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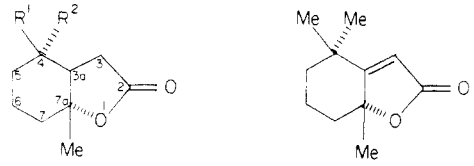
Received August 13, 1984

A new chemical route for a facile resolution of racemates of trans-fused γ-lactones is presented. The method has been applied to the resolution of natural lactones anastrephin (**1a**) and epianastrephin (**1b**) and their three analogues **1c–e**. Racemic lactones **1** are reacted with (*R*)-(−)-α-phenylglycinol to give diastereomeric hydroxy amides **4**, which can easily be separated by using standard, low-pressure, silica gel chromatography. A mild base hydrolysis of **4** to produce hydroxy acids **5** is followed by regeneration of the lactone function. The lactones are assigned absolute configuration by application of NMR, optical, and chemical methods. The latter approach includes a stereospecific synthesis of (+)-*trans*-tetrahydroactinidiolide (**1d**) and (−)-dihydroactinidiolide (**1g**). A new stereoselective and efficient synthesis of (±)-**1d** is also presented.

Anastrephin (**1a**) and epianastrephin (**1b**) are major components of the male sex pheromone of both Caribbean, *Anastrepha suspensa* (Loew), and Mexican, *Anastrepha ludens* (Loew), fruit flies. The structures and relative configurations of these lactones have been established in this laboratory using chemical methods[2,3] and by others using an X-ray diffraction method.[4] We have shown that the natural lactones isolated from cultured *A. suspensa* males are not single enantiomers, although each is enantiomerically enriched. Application of the chiral NMR shift reagent has indicated enantiomeric excess in the range 55 ± 3 (−)/45 ± 3 (+) for both lactones **1a** and **1b** and suggested the 3a*S*,7a*S* configuration of the major (−) enantiomers.[2]



1a, R^1 = $CH{=}CH_2$, R^2 = CH_3

1b, R^1 = CH_3, R^2 = $CH{=}CH_2$

1c, R^1R^2 = CH_2CH_2

1d, $R^1{=}R^2$ = CH_3

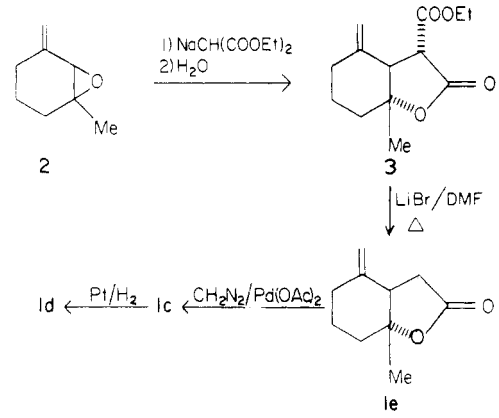
1e, R^1R^2 = CH_2

1f, R^1 = CH_3, R^2 = H

1g

In this paper we report a facile resolution of enantiomers of anastrephin and epianastrephin as well as confirmation of the previously suggested configurational assignments. In addition, we present the synthesis, resolution, and determination of the absolute stereochemistry of three analogues, **1c–e**, of these natural lactones, as well as the stereospecific transformation of optically active lactone **1e** into other lactones, namely, *trans*-tetrahydroactinidioilide[5] (**1d**), lactone **1f**, and dihydroactinidiolide[6-8] (**1g**). In spite of considerable interest in *trans*-tetrahydroactinidiolide, this compound has not been reported before in an optically active form.

Scheme I



Besides the intrinsic interest in development of a new methodology for a facile resolution of enantiomeric lactones, the optically active compounds, which are reported here, can serve as valuable probes in the investigation of the structure of the pheromone receptors in the species of *A. suspensa* and *A. ludens* flies. Bioassays of these

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(2) Battiste, M. A.; Strekowski, L.; Vanderbilt, D. P.; Visnick, M.; King, R. W.; Nation, J. L. *Tetrahedron Lett.* **1983**, *24*, 2611.

(3) Visnick, M. Ph.D. Dissertation, University of Florida, 1983.

(4) Stokes, J. B.; Uebel, E. C.; Warthen, J. D.; Jacobson, M.; Flippen-Anderson, J. L.; Gilardi, R.; Spishakoff, L. M.; Wilzer, K. R. *J. Agric. Food Chem.* **1983**, *31*, 1162.

(5) For syntheses of (±)-*trans*-tetrahydroactinidiolide, see: (a) Hoye, T. R.; Caruso, A. J.; Kurth, M. J. *J. Org. Chem.* **1981**, *46*, 3550. (b) Hoye, T. R.; Kurth, M. J. *Ibid.* **1979**, *44*, 3461. (c) Hoye, T. R.; Kurth, M. J. *Ibid.* **1978**, *43*, 3693. (d) Saito, A.; Matsushita, H.; Tsuino, Y.; Kisaki, T.; Kato, K.; Noguchi, M. *Chem. Lett.* **1978**, 1065. (e) Matsumoto, T.; Sakata, G.; Tachibana, Y.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1147.

(6) For syntheses of the enantiomers of dihydroactinidiolide, see: (a) Mori, K.; Nakazono, Y. *Tetrahedron* **1986**, *42*, 283. (b) Isoe, S.; Hyeon, S. B.; Katsumura, S.; Sakan, T. *Tetrahedron Lett.* **1972**, 2517. (c) Kienzle, F.; Meyer, H.; Minder, R. E.; Thommen, H. *Helv. Chim. Acta* **1978**, *61*, 2616. (d) Eschenmoser, W.; Uebelhart, P.; Eugster, C. H. *Ibid.* **1982**, *65*, 353.

(7) For a review on the synthesis of (±)-dihydroactinidiolide, see ref 6a.

(8) For a review on the isolation of racemic or enantiomerically enriched dihydroactinidiolide from natural sources consult ref 6a.

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