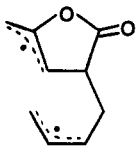

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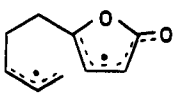

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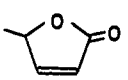

6

ygen lone pair and one each from the four ring carbons). To illustrrate this point, we have calculated the bond dissociation energy of the annular C–H bond in the 5-methyl-2(5*H*)-furanone (β-angelica lactone, **6**). This value of 78.0 kcal/mol is significantly less than the corresponding calculated value (89.7 kcal/mol) for the benzylic hydrogens in toluene and lower than any of the similarly calculated bond dissociation energies of the benzylic C–H's of any of the possible α and/or para cyano- or hydroxy-substituted toluenes.[19] The result also agrees with the experimental observation that protoanemonin can dimerize to form a [2+2] adduct, presumably via an analogous biradical intermediate.

Some difference of opinion has been expressed in the literature about the use of CI with AM1 and MNDO calculations. Dewar has suggested that CI artifactually lowers the energy of biradicals by about 15 kcal/mol.[10f] However, many calculations using MNDO or AM1 and CI on the rearrangement of semibullvalenes,[20] bond thermolysis of azoalkanes,[21] radical recombinations of carbon- and nitrogen-centered radicals,[22] and recombination of benzyl radicals[23] have been remarkably successful both qualitatively and quantitatively. A study of bond dissociations of small molecules using MNDO/CI gave reaction profiles similar to MP4 and MCSCF ab initio calculations, even when CI up to 136 × 136 was used.[24]

Dewar has also noted that, without CI, AM1 RHF calculations cannot account for the rate-enhancing effects of substituents on the dienophile, such as cyano.[10f]

The results presented here suggest that the experimentally observed site selectivity in the Diels–Alder reaction between protoanemonin and butadiene can be better understood by invoking either a highly asynchronous or two-step mechanism. The ability of protoanemonin to form a cyclic, aromatic radical (as part of a biradical) upon attack by butadiene at the exocyclic methylene group is probably the determining factor in the observed selectivity.

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**Registry No.** Protoanemonin, 108-28-1; butadiene, 106-99-0.

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# Formation of a Chiral 1-Fluoro-2,2-diphenylcyclopropyl Radical in the Barton Decarboxylation Reaction†,1

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The chiral 1-fluoro-2,2-diphenylcyclopropyl radical (**8**), generated in the Barton decarboxylation reaction, was used as a probe to evaluate a variety of halogen and hydrogen atom donating reagents as radical traps.

The thermal decomposition of *N*-hydroxypyridine-2-thione esters to produce radicals which can react with a variety of halogen-donating reagents resulting in an halogenative decarboxylation reaction or with H-atom donating sources to give rise to products of decarboxylation has been given the appellation, Barton decarboxylation reaction.[2] In an ancillary study the need arose to prepare chiral 1-bromo-1-fluoro-2,2-diphenylcyclopropane (**1**), and the Barton decarboxylation reaction was selected to carry out the conversion of the available[3] chiral 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid (**2**) to the desired **1**.

There exists a large body of evidence[4] that shows, barring large steric interactions,[5] that the cyclopropyl radical is a rapidly inverting ($10^{11}$–$10^{12}$ $s^{-1}$ at 71 °C) bent σ radical[6] incapable of maintaining its configuration. However, electronegative substituents in the α-position, such as fluorine or alkoxy, are known to slow down the inversion frequency to the extent that if a very good radical trap is

†This article is dedicated to Professor Derek H. R. Barton in recognition of his many important contributions to organic chemistry.
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(1) This work was supported by a grant from the National Science Foundation for which we are grateful.
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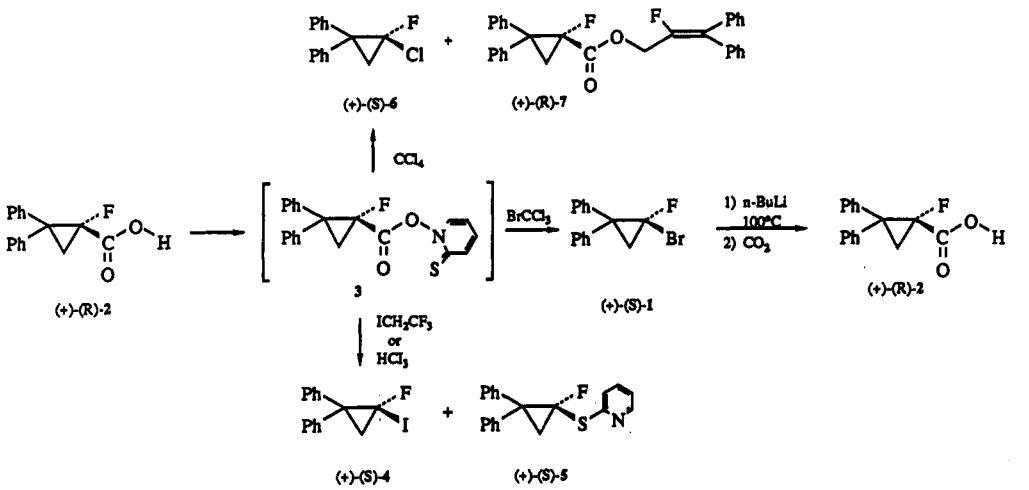
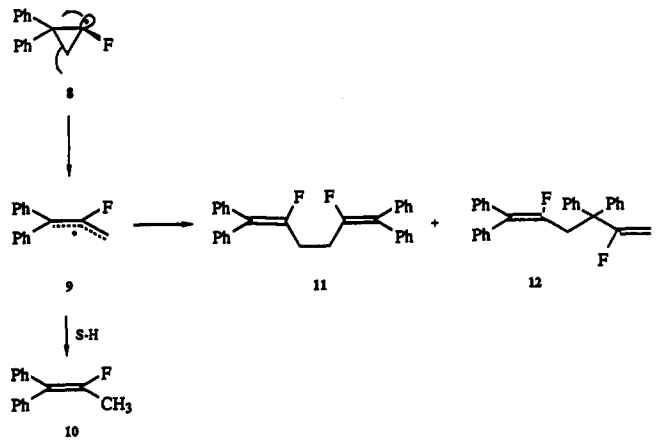
Scheme I



available then the radical can partially or completely maintain its configuration.[4] The inversion frequency for an $\alpha$-fluorocyclopropyl radical has been estimated[7] to be $10^6$ $s^{-1}$ at −108 °C, and the inversion barrier has been calculated[8] (CNDO/2) to be 10.5 kcal·mol$^{-1}$.

**Halogenative Decarboxylation.** Chiral acid,[9] (+)-(*R*)-**2**, was converted to its acid chloride[9] (oxalyl chloride/DMF) which was then treated with sodium 2-mercaptopyridine *N*-oxide and a catalytic amount of DMAP to form the thione ester **3** in situ. The thermal decomposition of **3** in the presence of an excellent radical trap such as $BrCCl_3$ produced (+)-(*S*)-**1** in 78% yield. The reaction was shown to have occurred, as anticipated, with complete retention of configuration. This was established by converting the isolated (+)-(*S*)-**1**, $[\alpha]^{24}_D$ +200°, back to the optically pure (+)-(*R*)-**2** by a series of reactions that are known to proceed with complete retention of configuration;[10] halogen–metal exchange of **1** with a pentane solution of *n*-butyllithium at −100 °C followed by carbonation.

The thermolysis of **3** in the presence of an excess of 2-iodo-1,1,1-trifluoroethane, as an iodine source[11] for radical **8**, gave only a 5% yield of (+)-(*S*)-1-fluoro-1-iodo-2,2-diphenylcyclopropane (**4**) whose optical purity was 72% and a 16% yield of (+)-(*S*)-**5** with an optical purity of 75%. The latter compound results from the reaction of **8** with the 2-thiopyridyl radical that is formed in the decomposition of **3**. (+)-(*S*)-**5** was prepared in optically pure form by the addition of 2-pyridine disulfide to a solution of 1-fluoro-2,2-diphenylcyclopropyllithium, prepared by the reaction of *tert*-butyllithium with (+)-(*S*)-**4** at −100 °C. Moreover, as is typical of cyclopropyl radicals[4,12] when a very good radical trap is not available, the radical **8** can undergo ring opening to the more stable allyl radical **9**. In this case radical **9** can dimerize to give **11** (head-head) and **12** (head-tail). By contrast, in the presence of very good radical trap such as bromotrichloromethane (vide supra), **8** not only maintains its configuration completely but its structural integrity as well, since none of the products resulting from ring opening (**10–12**) are observed. Evidently, iodoform is also an excellent radical trap since the decomposition of **3** in its presence gave a 56% yield of optically pure[9,10] (+)-(*S*)-**4**, and no ring-opened products could be detected.



The in situ formation and thermolysis of **3** in carbon tetrachloride gave only a 5% yield of (+)-(*S*)-1-chloro-1-fluoro-2,2-diphenylcyclopropane (**6**) with an optical purity of 83%. The optical purity of **6** was established by preparing it in optically pure form by the addition of trifluoromethanesulfonyl chloride to a solution of (1-fluoro-2,2-diphenylcyclopropyl)lithium, prepared as described above. The major product from the thermolysis was recovered acid **2** which indicates that **3** was either not formed at all (2-mercaptopyridine was also isolated) or that not all the acyloxy radical produced in the thermolysis of **3** decarboxylated to form **8**. That the latter occurred was indicated by the isolation of (+)-(*R*)-**7**, which was undoubtedly formed by the combination of the acyloxy radical with the ring-opened radical **9**. In a separate experiment **3** was prepared independently and in quantitative yield using phase-transfer conditions (see the Experimental Section) and then subjected to photolytic (tungsten lamp) decomposition in carbon tetrachloride. The results were comparable to those when **3** was formed in situ, (+)-(*S*)-**6** was isolated in 9% yield with an optical purity of 80%.

**Decarboxylation.** To obtain the corresponding hydrocarbon in the Barton decarboxylation reaction a very good H-atom source is essential. Newcomb and Park[13]

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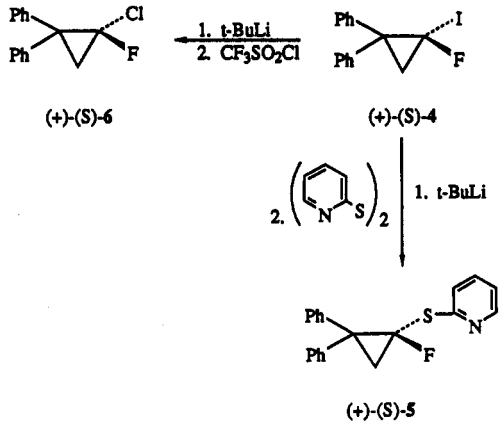
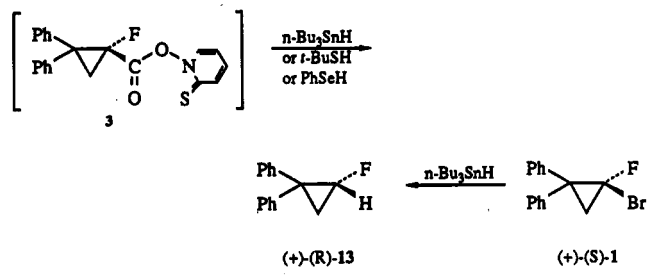



(+)-(S)-6 (+)-(S)-4 (+)-(S)-5

have recently made an evaluation of such sources in this reaction and found, inter alia, that *tert*-butyl mercaptan $\simeq$ *n*-$Bu_3SnH$ >>> THF in their ability to donate a H-atom to a carbon-centered radical. The observation that the cyclopropyl radical **8** generated either by the thermal decomposition of **3** using *tert*-butyl mercaptan or *n*-$Bu_3SnH$ as radical traps or by the thermal decomposition of the *tert*-butyl perester[9] of chiral **2** in THF resulted in formation of (+)-(*R*)-**13** with optical purities of 84%, 83%, and 47%, respectively. These results are in line with the




3

(+)-(R)-13 (+)-(S)-1

findings of Newcomb and Park. Also, in each case, ring-opened product is found and this is in contrast to the results, no opened product and 100% optical purities, that are observed when superior radical traps such as bromotrichloromethane or iodoform are used. In order to obtain complete retention of optical activity and configuration in the decarboxylation reaction it is necessary to use either benzenethiol or benzeneselenol as radical traps. The use of these reagents give rise to optically pure **13** in yields of 38% and 8%, respectively. Obviously, benzenethiol is the radical trap of choice. The low yields obtained are largely due to a transesterification reaction with **3** to yield 48% of the benzeneselenol ester and 18% of the benzenethiol ester of (+)-(*R*)-**2**. Moreover, as in the cases of bromotrichloromethane and iodoform, no ring-opened products are found.

However, it should be noted that when **8** is generated from its precursor (+)-(*S*)-**1** with *n*-$Bu_3SnH$ a 65% yield of optically pure (+)-(*R*)-**13** is obtained, and no ring-opened products could be detected. This is in spite of the fact that the conditions, concentration and temperature, were the same as in the Barton reaction. The reason for this apparent leaving group effect is not clear.

## Experimental Section

All melting points and boiling points are uncorrected. $^1H$ NMR were recorded at 300 MHz using $CDCl_3$ as solvent unless noted otherwise, with $Me_4Si$ as internal standard.

Optical rotations were measured at the 546.1-nm mercury line on a Bendix-Ericson Model 987 ETL/NPL polarimeter equipped with a Bendix Model DR-1 digital display or a Thorn Emi-NPL Automatic Polarimeter Type 243. The cell length was 0.4 dm and the accuracy was ±0.002°. Ultraviolet (UV) spectra were recorded on a Cary 219 spectrophotometer.

Column chromatography was carried out by using either silica gel (70–230 mesh, Merck) or activated alumina F-20 (80–200 mesh). Radial chromatographic separation were performed with Merck silica gel 60 $PF_{254}$.

All bulk solvents were distilled before use. Diethyl ether, dimethoxyethane, and THF were dried by refluxing and distilling from sodium benzophenone.

**(+)-(*S*)-1-Bromo-1-fluoro-2,2-diphenylcyclopropane (1).** A solution of 4.7 g of optically pure (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride,[9] mp 98–102 °C, in 10 mL of freshly distilled bromotrichloromethane was syringed into a refluxing mixture of sodium 2-mercaptopyridine *N*-oxide (2.8 g; dried by azeotropic distillation with benzene), 25 mL of bromotrichloromethane, and 20 mg of DMAP. After refluxing for 1.5 h, the mixture was diluted with dichloromethane, washed with water, 2 N HCl, water, and 1 M sodium carbonate. After drying ($MgSO_4$) and removal of solvents, the residue was purified by short column chromatography on silica gel by elution with hexane–dichloromethane (5:1) to give 3.9 g (78%) of pure product; mp 72–73 °C; $[\alpha]^{24}_D$ +200.0°, $[\alpha]^{24}_{Hg}$ +232.5° (*c* 0.9, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 2.19 (1 H, dd, $J$ = 7.8, 28.4), 2.23 (1 H, dd, $J$ = 7.8, 38.0), 7.2–7.5 (10 H, m).

Anal. Calcd for $C_{15}H_{12}BrF$: C, 61.88; H, 4.15. Found: C, 61.81; H, 4.27.

That complete retention of configuration was obtained in the above reaction was demonstrated by conversion of the (+)-(*S*)-1-bromo-1-fluoro-2,2-diphenylcyclopropane, $[\alpha]^{24}_D$ +200°, to the known (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropanecarboxylic acid: A solution of the (+)-bromide (291 mg, 1 mmol) in 3 mL of THF and 2 mL of diethyl ether was treated at −100 °C with 0.7 mL of 1.6 M *n*-butyllithium in hexane. After 15 min, the solution was saturated with dry $CO_2$, hydrolyzed with water, and extracted with ether. The aqueous layer was acidified and extracted with ether, and the ether extracts were dried over anhydrous $MgSO_4$. Evaporation of the ether yielded 38 mg of the acid (**2**), $[\alpha]^{24}_D$ +121° (*c* 0.4, acetone).[9]

**(+)-(*S*)-1-Fluoro-1-iodo-2,2-diphenylcyclopropane (4). A.** A solution of 2.47 g (7 mmol) of (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride (benzene solvate) in 20 mL of hot benzene was added by syringe into a refluxing mixture of sodium 2-mercaptopyridine *N*-oxide (1.25 g, 8.4 mmol), 25 mL of benzene, 1.7 mL (17.3 mmol) of 2-iodo-1,11-trifluoroethane, and DMAP (50 mg). The mixture was refluxed and irradiated with a 500-W tungsten lamp for 1 h. Usual workup followed by short column chromatography gave a 5% yield of (+)-(*S*)-1-fluoro-1-iodo-2,2-diphenylcyclopropane: mp 81–83 °C (from hexane); $[\alpha]^{24}_{Hg}$ +196° (*c* 1.0, $CHCl_3$, 72% optically pure); $^1H$ NMR ($CDCl_3$) $\delta$ 2.10 (1 H, dd, $J$ = 7.8, 9.9), 2.29 (1 H, dd, $J$ = 7.8, 19.8), 7.2–7.5 (10 H, m); MS M (100) 211.

Anal. Calcd for $C_{15}H_{12}FI$: C, 53.27; H, 3.58. Found: C, 53.36; H, 3.61.

Other products isolated were **2,5-difluoro-1,1,4,4-tetraphenyl-1,5-hexadiene (12)** and **2,5-difluoro-1,1,6,6-tetraphenyl-1,1,6,6-tetraphenyl-1,5-hexadiene (11)**[9] (1:1.6 by NMR), yield 31%, and **(+)-(*S*)-1-fluoro-1-(2′-pyridylthio)-2,2-diphenylcyclopropane (5)** (16%): mp 109–112 °C (from ethyl acetate–hexane); $[\alpha]^{24}_{Hg}$ +211.0° (*c* 1.0, $CHCl_3$, 75% optical purity); $^1H$ NMR ($CDCl_3$ $\delta$ 2.22 (1 H, dd, $J$ = 6.6, 8.1), 2.33 (1 H, dd, $J$ = 6.6, 15.3), 7.1–7.4 (10 H, m), 7.5–7.7 (3 H, m), 8.50 (1 H, m); MS $M^+$ 321, M (100) 112.

Anal. Calcd for $C_{20}H_{16}FNS$: C, 74.78; H, 5.02. Found: C, 74.68; H, 5.11.

Optically pure (+)-(*S*)-**5** was prepared by treating a solution of optically pure (+)-(*S*)-**4** (108 mg, 0.32 mmol) in THF (2 mL) and ether (2 mL) with 1.7 M *tert*-butyllithium in pentane (0.42 mL, 2.2 equiv) at −100 °C. After 10 min a THF (2 mL) solution of 2-pyridine disulfide (106 mg, 0.48 mmol) was added, and the mixture was allowed to come to ambient temperature. Standard workup, followed by chromatography on silica gel, afforded **13** (eluted with $CH_2Cl_2$–hexane, 4:1, yield 21 mg, 30%) and **5** (eluted with $CH_2Cl_2$, yield 65 mg, 63%). One recrystallization of **5** from hexane gave mp 113–114 °C and $[\alpha]^{25}_{Hg}$ +281° (*c* 0.4, $CHCl_3$).

**B.** The solid (1.03 g, 2.92 mmol) of optically pure (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride (benzene solvate) was gradually added to a refluxing mixture of sodium 2-mercaptopyridine *N*-oxide (0.54 g, 3.3 mmol), iodoform (2.6 g,

6.6 mmol), DMAP (50 mg), and 30 mL of cyclohexene. Refluxing was continued for 3 h, and the solution, after cooling, was filtered through a short column of silica gel. The filtrate was evaporated in vacuo, and the residue (1.75 g) was triturated with warm hexane, leaving behind the unreacted iodoform (0.8 g). The hexane solution was chromatographed on a short column of silica gel to give 0.55 g (56% yield) of product, mp 84.5 °C, $[\alpha]^{25}_{Hg}$ +280° (c 1.0, $CHCl_3$).

Halogen-metal exchange of (+)-(S)-4, $[\alpha]^{25}_{Hg}$ +280°, with 2 equiv of *tert*-butyllithium at −110 °C followed by carbonation as described for (+)-(S)-1 above, gave a 65% yield of (+)-(R)-2, $[\alpha]^{24}_{Hg}$ +152° (c 1.0, actone, 100% optically pure[9]).

**(+)-(S)-1-Chloro-1-fluoro-2,2-diphenylcyclopropane (6). A.** A mixture of (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride (benzene solvate, 353 mg, 1 mmol), sodium 2-mercaptopyridine *N*-oxide (179 mg, 1.2 mmol), DMAP (10 mg), and freshly distilled carbon tetrachloride (15 mL) was sonicated at 32 °C (water bath) for 2.5 h. The reaction mixture was subjected to short column chromatography on silica gel (hexane–dichloromethane, 4:1, 1:1, and 100% dichloromethane). Final purification was performed by radial chromatography on silica gel to yield (+)-(S)-6 (13 mg, 5% yield): mp 74.5 °C; $[\alpha]^{25}_{Hg}$ +172° (c 0.13, $CHCl_3$, 83% optical purity); $^1H$ NMR δ 2.09 (1 H, dd, J = 7.2, 7.5), 2.23 (1 H, dd, J = 7.2, 16.2), 7.2–7.5 (10 H, m).

Anal. Calcd for $C^{15}H_{12}ClF$: C, 73.02; H, 4.90. Found: C, 73.05; H, 4.90.

Optically pure (+)-(S)-6 was prepared by the addition of 1.7 M *tert*-butyllithium in pentane (0.42 mL, 2.2 equiv) to a solution of (+)-(S)-4 (108 mg, 0.32 mmol) in 4 mL of a 1:1 mixture of THF and ether at −100 °C. After 10 min a 1-mL solution of 0.95 M trifluoromethanesulfonyl chloride in ether was added, and the reaction mixture was allowed to come to ambient temperature. A mixture of 13 and 6 was obtained from radial chromatography purification which was shown by NMR to consist of 23% 13 and 66% 6. The specific rotation of 6 was calculated to be $[\alpha]^{25}_{Hg}$ +209° (c 0.48, $CHCl_3$). Several recrystallizations of the mixture from hexane gave pure (+)-(S)-6, mp 82–83 °C and $[\alpha]^{25}_{Hg}$ +208° (c 0.33, $CHCl_3$).

**3,3-Diphenyl-2-fluoro-2-propenyl (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarboxylate (7)** (53 mg, 20% yield) was isolated in >90% purity (NMR) and gave $[\alpha]^{25}_{Hg}$ +86° (c 0.4, $CHCl_3$): $^1H$ NMR δ 2.13 (1 H, dd, J = 6.9, 18.0), 2.46 (1 H, dd, J = 6.9, 9.0), 4.50 (1 H, dd, J = 13.2, 21.0), 4.73 (1 H, dd, J = 13.2, 21.0), 7.0–7.5 (20 H, m); IR (neat) 1745, 1690, 1670, 1600, 1500, 1450, 1150, 775, 710 $cm^{-1}$. Saponification of 7 (2 N NaOH/methanol/reflux 3 h) yielded 2, 29 mg, mp 180–2 °C, and 3,3-diphenyl-2-fluoro-2-propen-1-ol (15 mg), oil purified by radial chromatography on silica gel (dichloromethane–hexane, 3:2): $^1H$ NMR δ 1.90 (1 H, t, J = 5.4), 4.27 (2 H, dd, J = 5.4, 21.9), 7.2–7.4 (10 H, m); IR (neat) 3540, 3340, 3040, 3015, 1660, 1600, 1500, 1450, 1205, 1040, 950, 780, 710 $cm^{-1}$; HRMS calcd for $C_{15}H_{13}OF$ 228.0950, found 228.0969.

Other products were 1,1-diphenylethylene (3 mg), 2,2′-dithiopyridine (28 mg), 2-mercaptopyridine *N*-oxide (50 mg), and 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid (100 mg).

**B. *N*-(2-Thioxopyridinyl) (+)-(R)-1-Fluoro-2,2-diphenylcyclopropanecarboxylate (3).** A mixture of (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride (benzene solvate, 0.96 g) and 0.5 g of sodium 2-mercaptopyridine *N*-oxide in 25 mL of dichloromethane, under nitrogen, was stirred overnight at ambient temperatures in the dark. The reaction mixture was filtered through a short column of silica gel, and the product was eluted with ether to yield 0.65 g (65%) of 3, mp 148–152 °C.

Unstable 3 (0.52 g) dissolved in 30 mL of carbon tetrachloride was indicated with a 500-W tungsten lamp for 1 h while cooling with a water bath (40 °C). Column chromatography on silica gel, followed by radial chromatography yielded: (+)-(S)-6 (32 mg, 9%) [$[\alpha]^{25}_{Hg}$ +167° (c 0.25, $CHCl_3$, 80% optical purity)]; 11 (27 mg, 7%), [mp 94–6 °C (from methanol); $^1H$ NMR δ 2.57 (4 H, dt, J = 6, 23), 7.07 (4 H, m), 7.15–7.35 (16 H, m); MS $M^+$ 422, M (100°) 211]; 12 (12 mg, 4%); (+)-(S)-5 (40 mg, 9%); (+)-(R)-2 (165 mg, 45%).

Anal. Calcd for $C_{30}H_{24}F_2$ (11): C, 85.28; H, 5.73. Found: C, 85.26; H, 5.73.

**(+)-(R)-1-Fluoro-2,2-diphenylcyclopropane (13). A.** A solution of 291 mg (1 mmol) of optically pure (+)-(S)-1-bromo-1-fluoro-2,2-diphenylcyclopropane, 870 mg (3 mmol) of freshly distilled tri-*n*-butyltin hydride, and 20 mg of AIBN dissolved in 5 mL of benzene was refluxed under nitrogen for 2.5 h, 10 mL of carbon tetrachloride was added, and reflux was continued for an additional hour. The solvents were evaporated, and to the residue was added a mixture of 20 mL of saturated aqueous potassium fluoride, 20 mL of dichloromethane saturated with iodine, and the mixture was stirred overnight. The reaction mixture was extracted with hexane, washed with 2 M solution of sodium thiosulfate, and dried over anhydrous $MgSO_4$, and the solvents were evaporated. The crude product was purified by short column chromatography on silica gel, and the hexane eluted fraction was finally purified by radial chromatography to yield 138 mg (65%) of pure product: oil; $[\alpha]^{24}_{Hg}$ +20.7° (c 1.25, $CHCl_3$); reported[9] $[\alpha]^{25}_{Hg}$ +16.2° (c 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 1.57 (1 H, dd, J = 6.3, 11.7), 1.79 (1 H, ddd, J = 3.2, 7.0, 22.8), 5.01 (1 H, ddd, J = 3.2, 6.3, 65.4), 7.15–7.45 (10 H, m).

**B.** A solution of 1.5 g (5 mmol) of (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride in 5 mL of toluene was syringed into a refluxing suspension of a mixture of anhydrous sodium 2-mercaptopyridine *N*-oxide (0.9 g, 6 mmol), 50 mg of DMAP, and 2.5 mL (22 mmol) of *tert*-butyl mercaptan dissolved in 25 mL of toluene. After refluxing for 3 h under nitrogen, the mixture of products was separated by short column chromatography on silica gel using as eluents hexane and hexane–dichloromethane (1:1). Individual products were further purified by radial chromatography to give the following.

**(+)-(R)-1-Fluoro-2,2-diphenylcyclopropane (13)** (200 mg, 19%), $[\alpha]^{24}_{Hg}$ +17.5° (c 0.8, $CHCl_3$, op 84%).

**1,1-Diphenyl-2-fluoropropene (10)** (30 mg): mp 47–8 °C; $^1H$ NMR ($CDCl_3$) δ 2.04 (3 H, d, J = 18), 7.2–7.4 (10 H, m); MS $M^+$ 212.

Anal. Calcd for $C_{15}H_{13}F$: C, 84.88; H, 6.17. Found: C, 84.70; H, 6.21.

**2,5-Difluoro-1,1,4,4-tetraphenyl-1,5-hexadiene (12)** (50 mg): mp 146.7 °C; $^1H$ NMR ($CDCl_3$) δ 3.36 (2 H, d, J = 20.5), 4.58 (1 H, dd, J = 3.3, 50.4), 4.84 (1 H, dd, J = 3.3, 19.8), 6.55 (2 H, m) 7.01 (2 H, d, J = 8.5), 7.1–7.3 (16 H, m); MS $M^+$ 422, M (100) = 211.

Anal. Calcd for $C_{30}H_{24}F_2$: C, 85.28; H, 5.73. Found: C, 85.34; H, 5.87.

***tert*-Butyl (+)-(R)-1-fluoro-2,2-diphenylcyclopropanethiocarboxylate** (100 mg): mp 119.20 °C; $[\alpha]^{24}_{Hg}$ +230.5° (c 0.5, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 1.42 (9 H, s), 2.09 (1 H, dd, J = 6.6, 18.0), 2.46 (1 H, dd, J = 6.6, 9.6), 7.1–7.5 (10 H, m); MS $M^+$ 328, M (100) 191.

Anal. Calcd for $C_{20}H_{21}FOS$: C, 73.14; H, 6.44. Found: C, 73.07; H, 6.47.

**C.** To a refluxing mixture of anhydrous sodium 2-mercaptopyridine *N*-oxide (0.9 g, 6 mmol) and 50 mg of DMAP in 25 mL of benzene was added by syringe a solution of (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride (1.5 g, benzene solvate) in 10 mL of benzene, followed by a solution of 4.0 g (13.7 mmol) tri-*n*-butyltin hydride and 0.1 g of AIBN in 10 mL of benzene. After refluxing for 3 h, under nitrogen, the reaction mixture was worked-up as described under **B** above to give (+)-(R)-1-fluoro-2,2-diphenylcyclopropane (225 mg, 25%), $[\alpha]^{24}_{Hg}$ +17.3° (c 0.8, $CHCl_3$, op 83%), 1,1-diphenyl-2-fluoropropane (100 mg), and 55 mg of a 1:2 mixture (NMR) of 2,5-difluoro-1,1,4,4-tetraphenyl-1,5-hexadiene (12) and 2,5-difluoro-1,1,6,6-tetraphenyl-1,5-hexadiene (11).

**D.** A solution of optically pure (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride (benzene solvate, 705 mg, 2 mmol) and tetrabutylammonium bromide (20 mg) dissolved in 5 mL of dichloromethane was stirred at 0 °C, in the dark, with a solution of sodium 2-mercaptopyridine *N*-oxide (360 mg, 2.4 mmol) dissolved in 2 mL of water. After 0.5 h the organic phase was separated, washed with water, and dried over $MgSO_4$, and the solvent was evaporated in vacuo. The yellow solid ester 3 (0.75 g) dissolved in benzene (10 mL) was combined with 1 g (Aldrich, 90%) of benzeneselenol dissolved in 4 mL of benzene, and the solution was refluxed for 0.5 h. The reaction mixture was diluted with ether, and extracted with 2 N NaOH and water, and dried over $MgSO_4$, and the solvent was evaporated. The reaction products were separated by a combination of short column and radial chromatography using hexane–dichloromethane (1:1 and

4:1) for elution to yield 35 mg (8%) of (+)-(*R*)-**13** [$[\alpha]^{24}_{Hg}$ +21° (*c* 0.3, $CHCl_3$, optically pure)] and 13 mg (2%) of 1-fluoro-1-(phenylseleno)-2,2-diphenylcyclopropane [mp 91–3 °C; $[\alpha]^{24}_{Hg}$ +221° (*c* 0.12, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 2.12 (1 H, dd, *J* = 7.2, 8.4), 2.16 (1 H, dd, *J* = 7.2, 14.4), 7.2–7.35 (11 H, m), 7.4–7.55 (4 H, m)].

Anal. Calcd for $C_{21}H_{17}FSe$: C, 68.66; H, 4.66. Found: C, 68.49; H, 4.68.

Phenyl (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropaneselenocarboxylate was isolated in 48% yield (0.38 g): mp 114–5°, $[\alpha]^{24}_{Hg}$ +339° (*c* 1.2, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 2.25 (1 H, dd, *J* = 6.6, 18.3), 2.47 (1 H, dd, *J* = 6.6, 9.3), 7.1–7.5 (15 H, m); IR (Nujol) 1710, 1500, 9.55 $cm^{-1}$.

Anal. Calcd for $C_{22}H_{17}FOSe$: C, 66.84; H, 4.33. Found: C, 66.73; H, 4.38.

**E.** A 10-mL benzene solution of ester **3** (2 mmol prepared as in **D** above) and 1 mL of thiophenol were refluxed for 0.5 h. The usual workup procedure afforded phenyl disulfide (0.35 g) (mp 57–8 °C; (+)-(*R*)-**13** (0.16 g, 38%) [$[\alpha]^{24}_{Hg}$ +21.0° (*c* 1.5, $CHCl_3$, optically pure)]; and phenyl (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropanethiocarboxylate (0.115 g, 18‰) [mp 103–4 °C (from hexane); $[\alpha]^{24}_{Hg}$ +402° (*c* 0.5, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 2.21 (1 H, dd, *J* = 6.9, 18.3), 2.50 (1 H, dd, *J* = 6.9, 9.6), 7.1–7.4 (13 H, m), 7.52 (2 H, d, *J* = 8); IR (Nujol) 1700, 1500, 970 $cm^{-1}$.

Anal. Calcd for $C_{22}H_{17}FOS$: C, 75.84; H, 4.92. Found: C, 75.82; H, 4.97.

# Absolute Rate Constants for the β-Scission Reaction of the 1-Phenyl-2-phenoxypropyl Radical: A Model for Radical Reactions of Lignin[1]

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Absolute rate expressions for β-scission of the phenoxy radical from the 1-phenyl-2-phenoxypropyl radical, forming *cis*- and *trans*-β-methylstyrene, were determined by competition of β-scission ($k_\beta$) with abstraction of hydrogen from trimethylstannane ($k_{abs}$). Relative rates ($k_\beta/k_{abs}$) were converted to absolute rates ($k_\beta$) by using a rate expression determined for abstraction of hydrogen atom from tributylstannane by the phenylethyl radical: $\log [k_{abs}/(M^{-1}\,s^{-1})] = (9.31 \pm 0.30) - (7.11 \pm 0.49)/\theta$, where $\theta = 2.303RT$ kcal/mol (errors are $2\sigma$). The resulting expressions for β-scission are $\log (k_{\beta,trans}/s^{-1}) = (13.45 \pm 0.26) - (16.94 \pm 0.52)/\theta$ and $\log (k_{\beta,cis}/s^{-1}) = (13.41 \pm 0.3) - (19.3 \pm 0.75)/\theta$. The basis rate expression for abstraction of hydrogen from tributylstannane by the phenylethyl radical was determined in a competition of abstraction ($k_{abs}$) with self-termination ($k_t$), using the Smoluchowski expression for self-reaction of phenylethyl radical: $\log [2k_t/(M^{-1}\,s^{-1})] = 11.93 - 3.112/\theta$. Combining the Arrhenius parameters with the enthalpy change for β-scission leads to activation barriers for addition of phenoxy radical to *trans*- and *cis*-β-methylstyrene of 5.2 and 6.6 kcal/mol, respectively.

## Introduction

A predominate structural cross-link in the macromolecular network of lignin is the aryl β-aryl ether linkage, -(ArOCCAr)-.[2] Solid-state NMR studies suggest that alkyl aryl ether linkages may be present in modest extent in low-rank coals.[3] A detailed understanding of the free-radical[4] and radical cation[5] chemistry of lignin is necessary for the design of new processes of pulp preparation,[5] the understanding of pathways of hydrothermal conversion of biomass and coal to useful products,[6] and understanding the process of coalification of lignocellulosic structure.[7] The thermal decomposition of model compounds[6] and polymers[7] containing known structural units of lignin or proposed structural links in coal under hydroliquefaction conditions is a valuable exercise since direct observation of structurally distinct reactions remains nearly impossible for coal and difficult for lignin. Under ideal circumstances, the global kinetics and kinetic reaction order of thermal decomposition reactions of model compounds containing linkages of relevance to lignin and coal structure can be reduced to the contributing individual stepwise rate constants. The careful studies by Poutsma and Dyer[8] and Gilbert and Gajewski[9] of the homogeneous thermal decomposition of 1,*n*-diphenylalkanes (*n* = 2–4) and the studies of Buchanan and co-workers of heterogeneous decomposition of similar structures bonded to silica surfaces[10] provide examples of successful reduction of global rates to individual contributing rates. However, even the early stages of thermal decompositions of nominally simple systems may involve multiple initiation and propagation steps and early participation of secondary reactions. For these cases, design of experiments to directly determine individual reaction steps is desirable. A recent model compound study[9] examined radical chain decomposition pathways for cleavage of the C–O bond in phenyl 2-phenylethyl ether, as a model of reactions of similar structures presumably in low-rank coals. A free-

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