an equivalent amount of glacial acetic acid (0.06 g). The reaction was monitored by NMR spectroscopy. At equilibrium (~1 h), a small amount of hemiacetal ester was formed; the equilibrium mixture was very similar to that obtained by reacting hemiacetal ester **2** with **3**.

A similar reaction was observed between glacial acetic acid (0.12 g) and 1,1-dibutoxyethane (0.35 g) in $CDCl_3$ (3 mL).

The reaction of di-*n*-butyl acetal with equal amounts of 2-propanol or *tert*-butyl alcohol with TFA catalysis (~1%) leads to the formation of mixed acetals. Product mixtures were not separated.

Reaction of a $CDCl_3$ solution of **1** with anhydrous HCl resulted in initial formation of α-chloro ether **4** followed by the formation of secondary products after several hours at room temperature.

Reaction of Hemiacetal Ester 2 with Acetic Acid. The reaction of hemiacetal ester **2** (1.0 g) with acetic acid (10 mL) was conducted under nitrogen at reflux. The progress of the reaction was monitored by NMR spectroscopy. The reaction is slow, but after ~48 h the hemiacetal ester was completely converted to acetate **5**. At room temperature (<24 h) no reaction is observed between hemiacetal ester **2** and acetic acid. However, at long reaction times (>48 h) some acetate formation is observed in the NMR spectrum.

Thermolysis reactions where acetic acid was retained in the mixture were conducted by heating a neat sample of the hemiacetal ester in a flask equipped with a condenser and thermometer under nitrogen. The hemiacetal esters were only partially reacted (~25–50%) after ~24 h at 200 °C Under conditions where acetic acid is removed from the reaction mixture (attempted distillation), hemiacetal ester **2** is decomposed to give 2-phenoxyethyl vinyl ether.

Analysis of the reaction mixtures by gas chromatography was not possible due to partial decomposition of the hemiacetal ester under the analysis conditions.

Thermolysis of Hemiacetal Ester 6. A neat sample of **6**, prepared without TFA catalysis, was heated at 200 °C in a flask fitted with condenser and thermometer. Thermolysis under N_2 resulted in initial formation of acetal **1** followed by formation of 2-phenoxyethyl decanoate (**7**). The reaction was monitored by NMR spectroscopy. Reaction spectra were compared to those of authentic samples. After 2 h, ester **7** was the major reaction product (~85%).

Preparation of Phenoxyethyl Carboxylates 5 and 7. An authentic sample of **5** was prepared by refluxing 2-phenoxyethanol (13.8 g) with 10 mL of acetic anhydride in 50 mL acetic acid. The reaction was heated under N_2 for 6 h. The product was isolated by vacuum distillation; 10.7 g (59% yield).

2-Phenoxyethyl acetate (**5**): bp 84–85 °C (0.12 mm); IR 1740, 1595, 1495, 1220, 1060, 690 cm^{-1}; ^1H NMR δ 7.4–6.8 (m, 5 H), 4.5–4.1 (m, 4 H), 2.0 (s, 3 H); ^{13}C NMR 170.7, 158.8, 129.7, 121.2, 114.8, 65.9, 62.9, 20.5 ppm; mass spectrum, *m/e* (relative intensity) 180 (7), 120 (5), 107 (3), 94 (18), 87 (93), 77 (16); precise mass calcd 180.0786, found 180.0781. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.57; H, 6.83.

An authentic sample of **7** was prepared by adding a chloroform solution of decanonyl chloride (3.82 g) to a pyridine solution of 2-phenoxyethanol (2.76 g). The reaction mixture was stirred at reflux under N_2 overnight. The product was isolated by repeated aqueous extraction and purified by vacuum distillation; 5.3 g (90% yield).

2-Phenoxyethyl decanoate (**7**): bp 157–160 °C (0.15 mm); IR 2920, 2850, 1735, 1595, 1495, 1455, 1240, 1170, 690 cm^{-1}; ^1H NMR δ 7.3–6.8 (m, 5H), 4.4–4.1 (m, 4 H), 2.3 (t, 2 H), 1.8–1.1 (m, 14 H), 1.0–0.8 (m, 3 H); ^{13}C NMR 173.7, 158.6, 129.5, 121.2, 114.7, 66.0, 62.6, 62.6, 34.2, 31.9, 29.2, 25.0, 22.7, 14.1 ppm; precise mass calcd 292.2038, found 292.1999. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.96; H, 9.80.

Reaction of Hemiacetal Ester 2 with TFA or HCl. A $CDCl_3$ solution (5 mL) of **2** (0.10 g) was allowed to react with an equivalent amount of dry TFA (0.51 g). The NMR spectra showed complete conversion of **2** to 1-(2-phenoxyethoxy)ethyl trifluoroacetate and acetic acid.

In a similar experiment anhydrous HCl was bubbled into a $CDCl_3$ solution of **2** to give chloro ether **4**.

Reaction of 1,1-Diacetoxyethane (8) with Alcohols. Distilled 1,1-diacetoxyethane **8** (1.46 g) was allowed to react with either *n*-butanol (0.74 g) or 2-phenoxyethanol (1.38 g) in chloroform solution with a variety of catalysts (~1%; TFA, HCl, H_2SO_4, $BF_3{\cdot}OEt_2$, or tetraisopropyl titanate). In each case, conversion of alcohol to acetate was observed, with formation of acetaldehyde and acetic acid. At long reaction times (~24 h) high levels of conversion (>85%) were achieved. Often, trace amounts of acetal were observed, probably arising by reaction of alcohol with acetaldehyde.

Acknowledgment. P. Donahue recorded ^{13}C NMR spectra. Mass spectral analyses were performed by H. Grade. Helpful discussions with S. Danishefsky and J. E. Pickett are appreciated.

Registry No. **1**, 82337-98-2; **2**, 82337-99-3; **3**, 122-99-6; **4**, 82338-00-9; **5**, 6192-44-5; **6**, 82338-01-0; **7**, 23495-14-9; **8**, 542-10-9; TFA, 76-05-1; acetic acid, 64-19-7; 2-phenoxyethyl vinyl ether, 18370-86-0; decanoic acid, 334-48-5; 1-butoxyethyl acetate, 33931-54-3; *n*-butyl vinyl ether, 111-34-2; 1-(2-phenoxyethoxy)ethyl trifluoroacetate, 82338-02-1; 1,1-dibutoxyethane, 871-22-7; *n*-butanol, 71-36-3; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; decanoyl chloride, 112-13-0.

Configuration Determination of (*R*)-(−)-1,1,2-Triphenyl-3,3-dimethylbutane and the Stereochemistry of the Reaction of Benzhydryllithium with (*R*)-(+)-α-Phenylneopentyl Chloride

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A three-step synthesis of optically pure (*R*)-(−)-1,1,2-triphenyl-3,3-dimethylbutane from (*R*)-(−)-α-*tert*-butylphenylacetic acid has been accomplished. The synthesis of α-phenylneopentyl chloroformate from optically pure (*R*)-(+)-1-phenyl-2,2-dimethyl-1-propanol was followed by decomposition at 95 °C to give samples of (*R*)-(+)-1-chloro-1-phenyl-2,2-dimethylpropane having much higher optical purities ($[\alpha]^{21}_D$ +72°, +67°) than samples obtained with thionyl chloride ($[\alpha]^{21}_D$ +41°, +47°).

Previously, we reported kinetic results on the coupling reactions of triphenylmethyllithium and diphenylmethyllithium with neopentyl iodide, neopentyl bromide, and benzyl fluoride to produce hydrocarbon coupling products as shown in eq 1a–c.[1] For study of the stereochemistry of the coupling process, α-phenylneopentyl chloride (**6**) seemed to offer an ideal system for theoretical,

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0022-3263/82/1947-3521$01.25/0 © 1982 American Chemical Society

$$Ph_3CLi + XCH_2C(CH_3)_3 \xrightarrow[25\ ^\circ C]{THF} Ph_3CCH_2C(CH_3)_3 \quad (1a)$$
1 2 3

X = I and Br

$$Ph_2CHLi + XCH_2C(CH_3)_3 \xrightarrow[0\ ^\circ C]{THF} Ph_2CHCH_2C(CH_3)_3 \quad (1b)$$
4 2 5

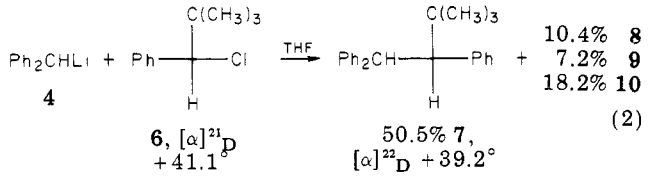
X = Br

$$Ph_3CLi + FCH_2C_6H_5 \xrightarrow[0\ ^\circ C]{THF} Ph_3CCH_2C_6H_5 \quad (1c)$$

as well as practical, reasons. On the one hand, it is structurally incapable of undergoing β elimination of HCl upon treatment with strongly basic organolithium reagents; on the other hand, chiral α-phenylneopentyl chloride[2] samples having substantial rotations can be prepared from 1-phenyl-2,2-dimethyl-1-propanol of known structure[3] and optical purity with thionyl chloride.[2]

Results

Diphenylmethyllithium (**4**) was reacted with (+)-1-chloro-1-phenyl-2,2-dimethylpropane (**6**) to give (+)-1,1,2-triphenyl-3,3-dimethylbutane (**7**) in 50.5% yield, as shown in eq 2, together with *meso*-α,α'-di-*tert*-butylbibenzyl (**8**), (+)-α,α'-di-*tert*-butylbibenzyl (**9**), and 1,1,2,2-tetraphenylethane (**10**).



(2)

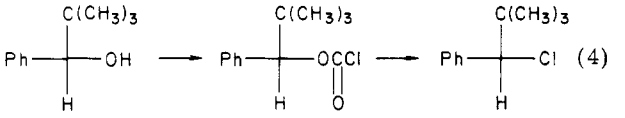
In order to determine the absolute configuration of (+)-**7** formed in eq 2, an authentic sample of chiral **7** was prepared from the known[4,9] (*R*)-(−)-α-*tert*-butylphenylacetic acid (**11**) by the reactions of Scheme I. Since the *R* isomer of **7** is levorotatory, the sample of (+)-**7** obtained in eq 2 is the *S* enantiomer. Furthermore, its optical purity is 20%. If the coupling process that produces **7** is stereospecific, the optical purity of **6** could be as low as 20%, and one can estimate a maximum value of 205° for the specific rotation of optically pure **6**. Conversely, if an alternative coupling process mechanism operates to produce **7**, for example, **4** + **6** = $Ph_2CHCl + PhCH(Li)C(CH_3)_3 \rightarrow$ **7**, or if an electron-transfer mechanism is operating, then completely racemic **7** would be expected.

The samples of (*R*)-(+)-**6** that were used in eq 2 were obtained by treating optically pure (*R*)-(+)-α-phenylneopentyl alcohol (**14**) with thionyl chloride in CCl_4 (see eq 3).[2]

(3)

14, $[\alpha]^{21}_D$ +30.9° **6**, $[\alpha]^{21}_D$ +41.1°

Our first approach to the problem of the optical purity of (+)-**6** was to synthesize it from (+)-**14** with phosgene rather than thionyl chloride. Phosgene reacts with alcohols to give alkyl chloroformates, which decompose with a higher S_Ni stereospecificity than alkyl chlorosulfites.[5-8] In practice, phosgene reacted with the lithium salt of (+)-**14** to form a moderately stable chlorocarbonate **14b**, which distilled in vacuo [bp 39–41 °C (0.05 mm)] with slight decomposition to (+)-**6** (see eq 4). The specific rotations



(+)-14 (+)-14b (+)-6 (4)

of α-phenylneopentyl chlorocarbonate (**14b**) and its related decomposition product, α-phenylneopentyl chloride, are collected in Table I, together with the % ee of the starting alcohol, **14**. Clearly, the best samples of (+)-**6** obtained with $SOCl_2$ have optical purities of 56 and 61% of those obtained using $COCl_2$.

The absence of precision between the observed specific rotation values for (+)-**6** suggested that the thermal decomposition at 95 °C of the neat samples of chlorocarbonate **14b** did not occur stereospecifically. Although no claim as to the optical purities of these samples can be made, one can feel confident that the assignment of the *R* configuration to (+)-α-phenylneopentyl chloride is correct because of retention of configuration during rearrangement of (*R*)-(+)-**14b** to (*R*)-(+)-**6**.

In addition, the observation of a significant amount of configuration inversion of (*R*)-(+)-**6** during the formation of (*S*)-(+)-**7** in eq 2 has motivated us to begin work on the problem of synthesizing optically pure α-phenylneopentyl

Scheme I

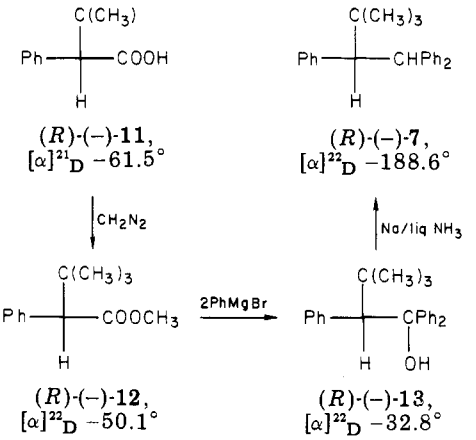


Table I. Specific Rotations of α-Phenylneopentyl Chlorocarbonate and α-Phenylneopentyl Chloride

run	$[\alpha]^{21}_D$, deg	ROH	% ee	$[\alpha]^{20}_D$, deg, **14b**[a]	$[\alpha]^{22}_D$, deg, (+)-**6**[b]
1	+31.1	acetone	100	+31.6	+67
2	+31.6	acetone	100	+32.3	+72

[a] In CCl_4. [b] In THF.

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Table II. Products of the Reaction of Diphenylmethyllithium with (+)-α-Phenylneopentyl Chloride

compd	col chromatography: wt, g (mmol)	% yield	mp, °C (lit.)	$[\alpha]^{22}_D$ (CCl_4), deg	VPC: wt, g (mmol)	% yield
$(CH_3)_3CCH(Ph)CH(Ph)C(CH_3)_3$ meso	0.125[a] (0.423)	7.24	183–184 (182)[13]		0.168	10.42
$PhCH(CMe_3)CH(CMe_3)Ph$	0.0284[b] (0.0964)	1.76	53–54	+19 ± 5 (c, 0.00186)	0.117 (0.396)	7.24
$PhCH(CMe_3)CHPh_2$	1.05[a] (3.34)	30.5	127–130	+39.2 (c, 0.1052)	0.174 (5.53)	50.5
$PhCH(Cl)C(CH_3)_3$					0.618 (3.39)	30.9
Ph_2CH_2					0.562 (3.34)	30.5

[a] After recrystallization from methanol. [b] After recrystallization from methanol at −78 °C.

chloride in an attempt to measure the selectivity of the predominant coupling process in eq 2.

Experimental Section

Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 B instrument equipped with a hydrogen flame ionization detector. Six-foot columns of $^1/_8$ in. diameter having either of two different packings were used. The packings were (1) 10% SE-30 on Chromsorb W (DMCS treated) and (2) 20% polyphenyl ether (5 ring) on Chromsorb W (DMCS treated). NMR spectra were obtained on a Varian T-60 spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 267 spectrophotometer. Rotations were observed with an O. C. Rudolph & Sons Model No. 70 polarimeter. Elemental analyses were done by Schwarzkopf Laboratories, Woodside, NY.

Resolution of α-*tert*-Butylphenylacetic Acid.[4,9] α-*tert*-Butylphenylacetic acid[12] (69.2 g, 0.36 mol) was mixed with 107.7 g of brucine dihydrate (0.25 mol) in warm methanol (1.9 L). Methanol (1 L) was distilled, and 115 g of salt, mp 96–106 °C was obtained. Two recrystallizations from methanol gave 70.5 g of salt: mp 112–130 °C; $[\alpha]^{21}_D$ −56.52° (c 0.0559, $CHCl_3$).

The foregoing salt was decomposed with 2 N HCl, and the resulting carboxylic acid was recrystallized from hexane to give 19.8 g of (−) acid: mp 141–142 °C; $[\alpha]^{21}_D$ −61.45° (c 0.0309, $CHCl_3$) [lit.[4a] mp 141–142 °C; $[\alpha]^{25}_D$ −62.9° (c 5, $CHCl_3$)].

The mother liquor of the first crop of resolution was concentrated and acidified with HCl to give 35 g of (+) acid. This acid was reacted with cinchonine (54 g, 0.18 mol) in 770 mL of warm methanol to which 250 mL of hot water was added. The salt that deposited on cooling was recrystallized twice from methanol/water (5:2) to give 29.4 g of solid: mp 194–200 °C; $[\alpha]^{21}_D$ +143.6° ($CHCl_3$, c 0.0424). Hydrolysis of this (+) salt by 2 N HCl, followed by recrystallization from hexane, gave 8.1 g of (+)-α-*tert*-butylphenylacetic acid: mp 140–141 °C; $[\alpha]^{28}_D$ +62.6° (c 0.0335 g/mL, $CHCl_3$). The best literature mp is 140.8–141.5 °C.[4,9]

Preparation of (*R*)-(−)-Methyl α-*tert*-Butylphenylacetate. Treatment of 18.7 g of (−)-α-*tert*-Butylphenylacetic acid [0.097 mol; mp 141–142 °C; $[\alpha]^{21}_D$ −61.45° ($CHCl_3$, c 0.0309)] with 0.2 mol of diazomethane (from *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide, Diazald) produced 16.7 g of (*R*)-(−)-methyl α-*tert*-butylphenylacetate (83%; mp 31–32 °C). Recrystallization from hexane at −20 °C gave 15.9 g of purified ester: mp 33–34 °C; $[\alpha]^{21}_D$ −50.12°, (c 0.0393, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.0 (s, 9 H), 3.5 (s, 1 H), 3.6 (s, 3 H), 7.26–7.6 (m, 5 H); IR 1735 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.83, 75.56; H, 8.76, 8.77.

Synthesis of (*R*)-(−)-1,1,2-Triphenyl-3,3-dimethylbutanol. Phenylmagnesium bromide was prepared from triply sublimed magnesium (2.33 g, 0.097 mol) and 13.75 g of bromobenzene (0.0875 mol) in THF. The (*R*)-(−) ester (3 g, 0.0145 mol, from the sample described above) in 30 mL of THF was added dropwise to the phenylmagnesium bromide. After the mixture was refluxed for 3 h, the reaction mass was stirred overnight and hydrolyzed with saturated NH_4Cl. Extraction into ether was followed by drying ($MgSO_4$) and distillation of the solvent to give 4.2 g of a solid, which was recrystallized from methanol to give 1.7 g of the title alcohol (31.2%): mp 168–171 °C; $[\alpha]^{21}_D$ −31.6° (c 0.0243, $CHCl_3$). Further purification by recrystallization improved the rotation to $[\alpha]^{21}_D$ −32.8° (c 0.0201, $CHCl_3$): NMR ($CDCl_3$) δ 0.85 (s, 9 H), 2.81 (s, 1 H), 4.00 (s, 1 H), 6.8–8.13 (m, 15 H); IR 3610, 3440 cm^{-1}. Anal. Calcd for $C_{24}H_{26}O$: C, 87.23; H, 7.93. Found: C, 86.70; H, 7.84.

Synthesis of (*S*)-(−)-1,1,2-Triphenyl-3,3-dimethylbutane. To 2.113 g (0.0064 mol) of the foregoing purified (*R*)-(−)-alcohol, 1.22 g of absolute ethanol, 20 mL of dry THF, and approximately 40 mL of liquid ammonia was added 0.882 g of sodium (0.0384 mol) in small pieces. The solution acquired a transient blue color; stirring was continued overnight at 25 °C. The residue was hydrolyzed with crushed ice and extracted into ether. After drying ($MgSO_4$) and solvent evaporation, the crude solid was recrystallized from methanol to give 0.9 g of crystals: mp 136–140 °C; $[\alpha]^{21}_D$ −156.2° (c 0.03067, CCl_4). Two successive recrystallizations from methanol did not completely purify the product. Column chromatography on alumina with hexane/benzene (99:1) gave 0.160 g of purified hydrocarbon: mp 149–150 °C; $[\alpha]^{21}_D$ −188.6° (c 0.01613, CCl_4). NMR ($CDCl_3$) δ 0.77 (s, 9 H), 3.65, 4.6 (q, J_{AB} = 11 Hz), 6.8–7.7 (m, 15 H). Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.13; H, 8.44.

Synthesis of Racemic 1,1,2-Triphenyl-3,3-dimethylbutanol. To 1.45 g of magnesium (0.06 mol) in 10 mL of THF was added 9.2 g of α-phenylneopentyl chloride (0.050 mol) in 10 mL of THF. After the addition was completed, the mixture was refluxed for 30 min, and 5.5 g of benzophenone (0.030 mol) was added. At the begining of the addition, a red color appeared, followed by a blue color which slowly disappeared. The reaction mixture was refluxed for 2 h, was left standing at 25 °C for 19 h, and was hydrolyzed. After the usual workup, 15.4 g of an oil was obtained. Crystallization at −20 °C from petroleum ether (30–60 °C) gave 5.3 g of crude racemic alcohol, mp 142–146 °C (53.5%). Recrystallization from methanol improved the sample's purity, mp 148–152 °C. The NMR spectrum of this alcohol was indistinguishable from that for the (*R*)-(−)-alcohol.

Synthesis of 1,1,1-Triphenyl-3,3-dimethylbutane. Neopentyl iodide (5.000 g, 25.25 mmol, in 10 mL of THF) was added to 17.12 mmol of triphenylmethyllithium in 100 mL of THF at 0 °C. After 20 min at 0 °C, the reacting mixture was warmed to 25 °C during 2 h, and reaction was terminated with methyl iodide (5.0 g, 36 mmol) to derivatize the remaining tritylithium. VPC showed the presence of four compounds; triphenylmethane (1.98 g, 8.13 mmol), triphenylethane (0.284 g, 1.09 mmol, 6.13%), neopentyl iodide (2.08 g, 10.50 mmol, 40%), and 1,1,1-triphenyl-3,3-dimethylbutane (4.54 g, 14.43 mmol, 84.3%).

Addition of diethyl ether (50 mL) was followed by extraction with 50 mL of saturated aqueous ammonium chloride, drying of the organic phase, distillation of the ether in the rotary evaporator, and chromatography of the residue (9.5 g) on 75 g of alumina using 1.5 L of hexane. Evaporation of early eluate fractions, followed by trituration of the oil with ethanol, gave 2.27 g (7.4 mmol, 42.3%) of pure 1,1,1-triphenyl-3,3-dimethylbutane: mp 103–104 °C (uncorr) (lit.[10] mp 102–103 °C); NMR ($CDCl_3$) δ 7.8–7.0 (m, 15 H), 2.9 (s, 2 H), 1.6 (s, 9 H). Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.35; H, 8.26.

An additional 2.08 g of the new hydrocarbon was isolated from later fractions but was contaminated with triphenylmethane and triphenylethane.

Synthesis of 1,1-Diphenyl-3,3-dimethylbutane. A mixture of diphenylmethyllithium (6.7 mmol) and neopentyl bromide (1.511 g, 10.0 mmol) in 50 mL of THF was stirred at 25 °C for

(12) One of us (D.A.B.) experienced a skin sensitivity to (±)-α-*tert*-butylphenylacetic acid in the form of a rash.

(13) Petrov, A. D.; Zak, E. P.; Zaveryrev, Y. M. *Zh. Obsch. Khim.* **1961**, *30*, 2838.

2 h. Purification and isolation by the method described above gave 1.411 g (5.95 mmol) of 1,1-diphenyl-3,3-dimethylbutane (89%): mp 33–33.5 °C (lit.[11] mp 33 °C); NMR ($CDCl_3$) δ 7.3 (m, 10 H), 4.1 (t, 1 H), 2.1 (d, 2 H), 0.9 (s, 9 H). Anal. Calcd for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.65; H, 9.48.

Synthesis of 1,1,1,2-Tetraphenylethane. The reaction of triphenylmethyllithium (9.0 mmol, in 50 mL of THF) and benzyl fluoride (1.101 g, 10.0 mmol) at 25 °C for 17 min gave 86.3% of 1,1,1,2-tetraphenylethane (2.598 g, 7.77 mmol) having properties identical with those described previously.

Run 2 at −78 °C. Triphenylmethyllithium (4.8 mmol in 20 mL of THF) was stirred with benzyl fluoride (.5286 g, 4.8 mmol) at −78 °C for 2 h. Termination with benzyl chloride (0.7 g, 5.5 mmol), followed by VPC, showed the presence of 72% unreacted benzyl fluoride (0.345 mmol), 1,1,1,2-tetraphenylethane (3.62 mmol, 75.4%), and 12.0% of stilbene (0.289 mmol), together with 3.2% of Ph_3CH (0.152 mmol).

Synthesis of (+)-α-Phenylneopentyl Chloride. (+)-α-Phenylneopentyl alcohol [3.00 g, 0.01827 mol; $[\alpha]^{21}_D$ +30.9° (c 0.03232, acetone)] in 10 mL of CCl_4 was added dropwise during 20 min to thionyl chloride (5.434 g, 0.04570 mol) at −5 °C. CCl_4 and unreacted $SOCl_2$ were distilled in vacuo and (+)-α-phenylneopentyl chloride distilled at 35–36 °C (0.05 mm), yielding 2.495 g (0.01366 mol, 75%) of chloride: $[\alpha]^{21}_D$ +41.1° (c 0.2002, THF); NMR ($CDCl_3$) δ 7.4 (m, 5 H), 4.7 (s, 1 H), 1.0 (s, 9 H).

Reaction of Diphenylmethyllithium with (+)-α-Phenylneopentyl Chloride. (+)-α-Phenylneopentyl chloride [2.000 g, 0.01095 mol; $[\alpha]^{21}_D$ +41.0° (c 0.2000, THF)] in 15 mL of THF was added during 15 min at 25 °C to diphenylmethyllithium (0.01095 mol in 15 mL of THF). This mixture was stirred for 2.5 days, and after workup with aqueous NH_4Cl and ether removal, the residue was triturated with 10 mL of hexane to yield 0.333 g of 1,1,2,2-tetraphenylethane (0.996 mmol, 18.2%). Analysis of the filtrate by VPC (6.0 ft, 10% SE-30/Chrom W, 300/220 °C, 95 mL/min), followed by chromatography over 250 g of alumina using a 95:5 hexane/benzene mixture, gave the results summarized in Table II.

Synthesis of (+)-α-Phenylneopentyl Chlorocarbonate. To a solution of 6.9 g of (R)-(+)-α-phenylneopentyl alcohol (0.0421 mol; $[\alpha]^{21}_D$ +31.1°; 0.0241 g/mL of acetone) in 80 mL of anhydrous ether was added 0.0429 mol of butyllithium in hexane. After stirring overnight at 25 °C, the alkoxide solution was added to a solution of phosgene (9.1 g, 0.091 mol) in 100 mL of dry ether at −60 °C. The mixture was warmed slowly to room temperature, became turbid, and was filtered to separate LiCl. Evaporation of the solvent left 8.8 g of a yellow liquid that was identified as α-phenylneopentyl chlorocarbonate (92% yield): NMR (neat) δ 0.87 (9 H, s), 5.51 (1 H, s), 7.26 (5 H, s); IR $\nu_{C=O}$ 1780 cm^{-1}; $[\alpha]^{21}_D$ +31.6° (0.0474 g/mL, CCl_4). The attempt to distill the crude chlorocarbonate gave a colorless liquid [bp 39–41 °C (0.06 torr) and 47–50 °C (0.2 torr)], which proved to be 46.5% chlorocarbonate and 53.5% (+)-6 by NMR analysis. Warming of this sample of chlorocarbonate at 95 °C completed the decomposition to yield crude (R)-(+)-α-phenylneopentyl chloride (3.7 g, 48%): $[\alpha]^{22}_D$ +67.0° (0.0248 g/mL, THF). The NMR spectrum was identical with that of a racemic sample of α-phenylneopentyl chloride.

Run 2. A comparably sized preparation produced 10.1 g of α-phenylneopentyl chlorocarbonate (90%): $[\alpha]^{20}_D$ +32.3° (0.05965 g/mL, CCl_4). Decomposition by heating in the absence of solvent at 100 °C for 2 h gave 4.7 g of (R)-(+)-α-phenylneopentyl chloride: $[\alpha]^{22}$ +72.0° (0.08943 g/mL, THF); n^{20}_D 1.5130. Anal. Calcd for $C_{11}H_{15}Cl$: C: 72.37; H, 8.28. Found: C, 71.92; H, 8.07.

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Registry No. (±)-α-*tert*-Butylphenylacetic acid, 13490-70-5; (−)-α-*tert*-butylphenylacetic acid brucine salt, 71185-51-8; (−)-α-*tert*-butylphenylacetic acid, 13491-16-2; (+)-α-*tert*-butylphenylacetic acid brucine salt, 71185-51-8; (+)-α-*tert*-butylphenylacetic acid, 13490-71-6; (R)-(−)-methyl α-*tert*-butylphenylacetate, 82372-89-2; (R)-(−)-1,1,2-triphenyl-3,3-dimethylbutanol, 82323-53-3; bromobenzene, 108-86-1; (S)-(−)-1,1,2-triphenyl-3,3-dimethylbutanol, 82323-54-4; (±)-1,1,2-triphenyl-3,3-dimethylbutanol, 82372-90-5; (±)-α-phenylneopentyl chloride, 82323-55-5; benzophenone, 119-61-9; 1,1,1-triphenyl-3,3-dimethylbutane, 24523-61-3; neopentyl iodide, 15501-33-4; triphenylmethyllithium, 733-90-4; triphenylethane, 5271-39-6; 1,1-diphenyl-3,3-dimethylbutane, 57123-34-9; diphenylmethyllithium, 881-42-5; neopentyl bromide, 630-17-1; 1,1,1,2-tetraphenylethane, 2294-94-2; benzyl fluoride, 350-50-5; (+)-α-phenylneopentyl chloride, 82323-56-6; (+)-α-phenylneopentyl alcohol, 23439-91-0; (+)-α-phenylneopentyl chlorocarbonate, 82323-57-7; *meso*-$(CH_3)_3CCH(Ph)CH(Ph)C(CH_3)_3$, 62678-51-7; $PhCH(CMe_3)$-$CH(CMe_3)Ph$, 27561-34-8; $PhCH(CMe_3)CHPh_2$, 82323-58-8; Ph_2CH_2, 101-81-5.

Nitrogen-15 Nuclear Magnetic Resonance and Photoelectron Spectroscopy of Substituted *N*-Phenylaziridines†

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^{15}N chemical shifts of ten *N*-arylaziridines were measured at the isotopic natural-abundance level. The values correlate well with ^{15}N and ^{17}O shifts in anilines and anisoles. The range of chemical shifts is consistent with decreased interaction between the lone pair and the benzene ring relative to anilines. Dual-substituent-parameter analysis of the shifts revealed a surprisingly high apparent resonance dependence. The steric effect of 2,6-dimethyl substitution on the ^{15}N resonance line positions was found to be much smaller than in dimethylanilines. Vertical ionization potentials for the three highest occupied orbitals were determined from photoelectron spectra. Attempts to correlate ionization potentials of lone-pair-like orbitals with ^{15}N shifts were unsuccessful; at best, a general trend exists between δ_N and only one of the ionization potentials. The lack of correlation was attributed to direct interactions between the lone-pair-like orbitals and the orbitals of the substituents that are not reflected in the nitrogen shifts.

The chemistry and bonding of small-ring organic molecules are of considerable interest to organic chemists. Numerous spectroscopic methods have been applied in this area, and nuclear magnetic resonance (NMR) spectroscopy has played an important role in these investigations. For nitrogen-containing compounds, ^{15}N NMR spectroscopy can be a particularly valuable experimental tool. For this purpose, it is important to establish the relationships between ^{15}N NMR parameters (chemical shifts, coupling

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