Alkylation of Allylic Derivatives. 12.[1] Stereochemistry of Copper(I)-Catalyzed Cross Coupling of Allylic Carboxylates with Grignard Reagents

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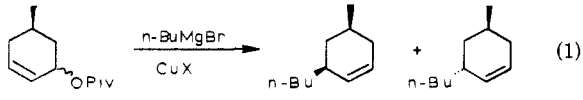
Alkylation of *cis*- and *trans*-5-methyl-2-cyclohexenyl pivalate (1-OPiv) with *n*-BuMgBr containing 1–2 mol % CuCN is stereospecific as well as completely regiospecific (exclusive γ-alkylation). The trans ester (*trans*-1-OPiv) gives *cis*-3-*n*-butyl-5-methylcyclohexene (*cis*-2) and the cis ester (*cis*-1-OPiv) gives *trans*-2. About 98% stereospecificity (anti) is observed with each isomer in this cyclic system. Regioselective alkylation of *trans*-α-methyl-γ-phenylallyl pivalate (5-OPiv) with *n*-BuMgBr containing 1 mol % CuCl gives α-alkylation with inversion of configuration. Regiospecific alkylation of 5-OPiv with *n*-BuMgBr containing 1 mol % CuCN gives anti-γ-alkylation. Both α- and γ-alkylation are completely stereospecific (within experimental error) in this acyclic system.

We recently reported that alkylation of allylic carboxylates with Grignard reagents containing catalytic amounts of cuprous salts has important advantages over conventional alkylations with stoichiometric amounts of preformed alkyl cuprates.[1] These advantages include greatly improved yields, especially with regard to the organometallic partner, and control of regiochemistry. With alkyl Grignard reagents containing 1–2 mol % CuCN, the reaction is highly regiospecific[2] and gives preponderant, if not exclusive, coupling at the γ-position. On the other hand, with other cuprous salts instead of CuCN, there is only a small amount of excess γ-alkylation.

Our initial study[1] was concerned with the scope of the reaction and the dependence of regiochemistry on the cuprous salt used as catalyst. We also observed that alkylation of *cis*-5-methyl-2-cyclohexenyl mesitoate (1-OTMB) with *n*-BuMgBr containing 10 mol % CuCN or CuCl gives *trans*-3-*n*-butyl-5-methylcyclohexene (2) (~97% trans isomer). This shows that in this case the reaction is either stereospecific or stereoselective—a distinction cannot be made with results for only one diastereomer. We have now investigated the stereochemistry of this catalytic process in the 5-methyl-2-cyclohexenyl (1) and α-methyl-γ-phenylallyl (5) systems and report the results in this paper.

The stereochemical results for alkylation of *cis*- and *trans*-5-methyl-2-cyclohexenyl pivalate (1-OPiv) with 2 equiv of *n*-BuMgBr containing 1 or 2 mol % CuCN are shown under eq 1. Our earlier study[1] showed that this reaction is completely regiospecific (γ-alkylation) and the present results show that the reaction is also highly stereospecific (anti alkylation favored).



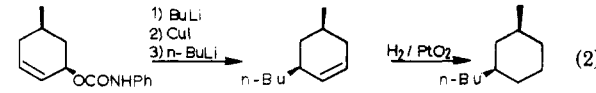
(1)

1-OPiv		*cis*-2	*trans*-2
99.5% *cis*-1	2% CuCN	2%	98%
98.0% *trans*-1	1% CuCN	96.5%	3.5%
98.0% *trans*-1	10% CuCl	96%	4%

These reactions were carried out in ether at 0 °C and the progress was monitored by periodic determination of the 1-OPiv/2 ratio by capillary GC. With 1 mol % CuCN the conversion of *trans*-1-OPiv to 2 was completed in <1 h. Under these conditions the reaction with *cis*-1-OPiv terminates at ~95% completion. An increase in the amount of CuCN to 2 mol % resulted in quantitative conversion to 2 in <1 h. In this system the trans isomer undergoes cross-coupling reactions somewhat faster than the cis isomer[3] which is the reason that more catalyst is required for the latter.

In this work it was found that CuCN is a much more effective catalyst than CuCl. With *trans*-1-OPiv, 10 mol % CuCl is required for ~98% conversion to 2 and reduction of the cuprous salt (black precipitate) is observed. Clearly, the number of catalytic cycles is much larger with CuCN (>50) than with CuCl (<5). As shown under eq 1, the stereochemistry is the same with 1% CuCN and 10% CuCl. The reaction of *cis*-1-OPiv with *n*-BuMgBr containing 10 mol % CuCl terminates at ~50% completion.

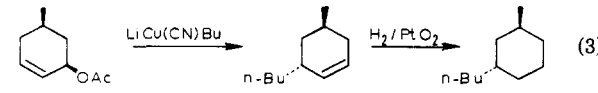
We, and others,[4] were unable to determine the configurational composition of 2 directly by capillary GC. Thus, product compositions were determined by hydrogenation (PtO_2) to 1-*n*-butyl-3-methylcyclohexane (4) and capillary GC analysis of the latter. Authentic samples of *cis*-2 and *trans*-2 and of the hydrogenation products, *cis*-4 and *trans*-4, were prepared by regio- and stereospecific methods developed earlier. As shown by eq 2, alkylation of *cis*-5-



(2)

3 *cis*-2 *cis*-4

methyl-2-cyclohexenyl-*N*-phenylcarbamate (3) with *n*-BuLi by a three-step process that results in exclusive syn γ-alkylation,[5] gave *cis*-2 which was converted to *cis*-4. Alkylation of *cis*-1-OAc with *n*-BuCu(CN)Li (anti γ-alkylation)[6] gave *trans*-2 which was converted to *trans*-4 as shown by eq 3.



(3)

cis-1-OAc *trans*-2 *trans*-4

It should be noted that alkylation of 1-OPiv is not completely stereospecific. With each isomer the anti/syn

(1) Previous paper in this series: Tseng, C. C.; Paisley, S. D.; Goering, H. L. *J. Org. Chem.*, preceding paper in this issue.

(2) The terms "regiospecific" and "regioselective" are used as defined in footnote 3 of: Goering, H. L.; Singleton, V. D., Jr. *J. Org. Chem.* **1983**, *48*, 1531.

(3) Goering, H. L.; Kantner, S. S.; Seitz, E. P., Jr. *J. Org. Chem.* **1986**, *51*, 5495.

(4) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318.

(5) Goering, H. L.; Kantner, S. S.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 715.

(6) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422.

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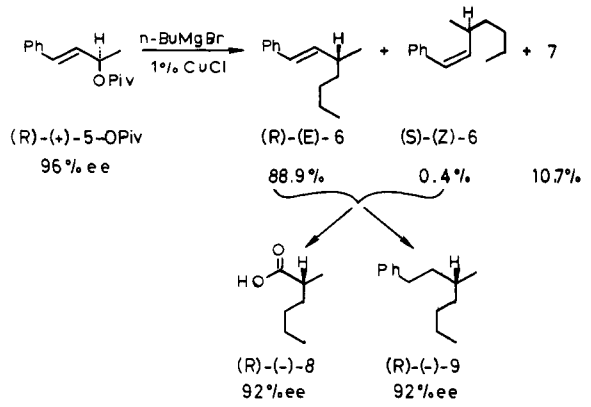
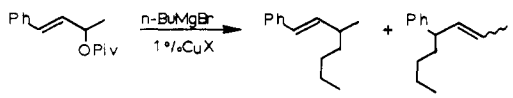
Scheme I. Stereochemistry and Regioselectivity for Alkylation of (*R*)-5-OPiv with *n*-BuMgBr Containing 1 Mole % CuCl



ratio is ~98/2. Put another way, anti stereochemistry is preferred but not required. The anti/syn ratio shows that the free energy of activation is about 2 kcal/mol less for anti alkylation than for syn alkylation in this cyclic system. The observed stereochemistry in this cyclic system is about the same as for stoichiometric alkylation of 1-OAc with $LiCuMe_2$[7] or LiCu(CN)Me.[6] Similar stereochemical results have been reported for cross coupling 2-cyclohexenyl methyl ethers with *n*-BuMgCl containing 5 mol % CuBr.[8]

The stereochemistry of alkylation of allylic derivatives with organometallic reagents is not always the same for cyclic and acyclic systems.[9] For this reason it was of interest to examine the copper(I)-catalyzed alkylation of α-methyl-γ-phenylallyl pivalate (**5**-OPiv) with *n*-BuMgBr. This acyclic system and reagent were chosen because the required absolute configurations and rotations are known.[5] Also, racemic samples of all of the components in the alkylation product were available from another study.[10]

Earlier[1] we showed that alkylation of **5**-OPiv with *n*-BuMgBr containing 1% CuCN or CuCl (eq 4)[11] gives high yields of isolated alkylation products. The reaction is highly regiospecific[2] with CuCN and gives ~97% of the γ-alkylation product **7** even though this system is biased in favor of the α-alkylation product **6**.[10] With 1 mol %



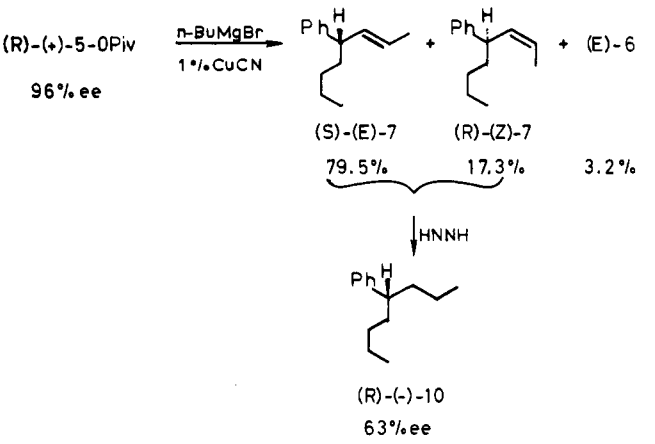
(4)

5-OPiv **6** **7**

CuCl, instead of CuCN, the reaction is regioselective[2] and gives ~90% of the thermodynamically favored α-alkylation product **6**. Thus CuCN is the catalyst of choice for investigating the stereochemistry of γ-alkylation, and in this biased system, CuCl is suitable for studying the stereochemistry of the **5**-OPiv → **6** transformation (α-alkylation).

Results for α-alkylation of (*R*)-(+)-**5**-OPiv with 2 equiv of *n*-BuMgBr containing 1 mol % CuCl are presented in Scheme I. The absolute configuration and rotation for **5**-OH, from which the pivalate was derived, have been established.[5] The composition of the alkylation product

Scheme II. Stereochemistry and Regiospecificity for Alkylation of (*R*)-5-OPiv with *n*-BuMgBr Containing 1 Mole % CuCN



was determined by capillary GC and components were identified by comparison of retention times with those of authentic racemic samples.[10] The configuration and optical purity of the α-alkylation product (*E*)-**6** was determined by a method developed previously which involves oxidation to α-methylhexanoic acid (**8**) of known absolute configuration and rotation.[12]

As shown in Scheme I, oxidation of a portion of the alkylation product derived from (*R*)-**5**-OPiv gave (*R*)-**8**. Thus α-alkylation proceeds with inversion of configuration. Moreover, the enantiomeric excess (ee) for **8** is within experimental error of that for the starting ester (**5**-OPiv). This shows there is little, if any, loss of optical configuration in the alkylation step.

Diimide reduction of a portion of the alkylation product, followed by preparative GC, gave a homogeneous sample of (-)-3-methyl-1-phenylheptane (**9**), $[\alpha]^{25}_D$ −8.55° (hexane). As shown in Scheme I, this has the same configuration and ee as (*R*)-**8**. Thus this experiment establishes that (-)-**9** has the *R* configuration and the absolute rotation for **9** is $[\alpha]^{25}_D$ 8.55°/0.92 = 9.29° (hexane).

The configuration of (*Z*)-**6** could not be determined and is insignificant because it is present in only trace amounts. However, for reasons outlined earlier,[12] we presume this product has the indicated *S* configuration and the same optical purity (ee) as the *E* isomer.

Results for γ-alkylation of (*R*)-(+)-**5**-OPiv with 2 equiv of *n*-BuMgBr containing 1 mol % CuCN are presented in Scheme II. The indicated product distribution was determined by capillary GC. Diimide reduction of the alkylation product gave a mixture from which the major component, 4-phenyloctane (**10**), was isolated in homogeneous form by preparative GC. The absolute configuration and rotation of **10** was established in earlier work.[5]

In this case the stereochemistry of γ-alkylation is complicated by the formation of both (*E*)- and (*Z*)-**7**. For reasons outlined elsewhere we presume that these isomers have opposite configurations and are of equal optical purity.[5,12] Diimide reduction converts these to enantiomers. Thus **10**, derived from a binary mixture of 82% (*E*)-**7** and 18% (*Z*)-**7**, will have the configuration corresponding to that of (*E*)-**7**, and the optical purity of **10** will be 36% less than that of (*E*)- and (*Z*)-**7**. As shown in Scheme II, **10** derived from the alkylation product has the *R* configuration and an ee of 63%. Thus (*E*)-**7** (major isomer) has the *S* configuration and (*Z*)-**7** (minor isomer) has the *R* configuration. The ee of these isomers, calculated from the

(7) Goering, H. L.; Singleton, V. D., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7854.
(8) Gendreau, Y.; Normant, J. F. *Tetrahedron* **1979**, *35*, 1517.
(9) Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1985**, *50*, 1597
(10) Goering, H. L.; Seitz, E. P., Jr.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304.
(11) This acyclic system undergoes cross-coupling reactions much faster than 2-cyclohexenyl systems (ref 3), and the reaction is quantitative with either 1 mol % CuCl or CuCN.
(12) Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 3986.

E/Z composition and the ee of the reduction product (R-10), is 63/0.64 = 98% which is within experimental error of that of the starting (R)-5-OPiv. Thus γ-alkylation, as well as α-alkylation (Scheme I), is highly stereospecific and involves anti bonding with little, if any, loss of optical configuration. The stereospecificity for α- and γ-alkylation by this catalytic method is higher than that observed earlier for stoichiometric alkylation of 5-OAc with LiCu(n-Bu)$_2$ (α-alkylation) and LiCu(CN)CH$_3$ (γ-alkylation).[12]

Evidently, the active alkylating species for the n-BuMgBr-CuCN combination is n-BuCu(CN)MgBr and that for catalysis by CuCl is (n-Bu)$_2$CuMgBr.[1] Presumably in each case the catalytic cycle[1] involves oxidative addition of the carboxylate to the cuprate with complete allylic rearrangement to give a S_N2' σ-allylcopper(III) complex. According to our mechanistic proposals[1,6] the stereochemistry of both α- and γ-alkylation is the same as that of the initial oxidative addition because all subsequent steps are thought to be stereospecific. It should be noted that the observed same stereospecificity (within experimental error) for α- and γ-alkylation is in agreement with this view. Evidently the stereochemistry of oxidative addition, and thus of alkylation, is controlled by steric factors. In sterically unbiased systems such as **5** or slightly biased systems such as **1**,[7] the anti side of the double bond is the least hindered side and anti stereochemistry for the S_N2' oxidative addition is favored.

Experimental Section

General Methods. All reagents were prepared and purified and Grignard solutions were standardized as reported earlier.[1] The high-resolution mass spectrometer and the NMR spectrometers used in this work have also been described.[1]

***trans*-5-Methyl-2-cyclohexenyl pivalate (*trans*-1-OPiv)** was prepared from *trans*-5-methyl-2-cyclohexenol (*trans*-1-OH)[13] and pivaloyl chloride in pyridine by a standard procedure.[1] Capillary GC (175 ft, UCON LB-550X, 120 °C) showed that this product contained 2% of the cis isomer. This product had the following: bp 100–105 °C (20 mm); IR (neat) 3045 (m), 2945 (s), 2900 (s), 2860 (s), 2820 (m), 1760 (s), 1480 (m), 1400 (m), 1288 (s), 1160 (s), 730 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.93–6.02 (ddd, 1 H, J = 2.2, 5.1, 9.9 Hz), 5.71–5.79 (br d, 1 H, J = 9.9 Hz), 5.19–5.22 (br s, 1 H), 1.00–2.20 (m, 14 H, t-Bu s at δ 1.19), 0.98 (d, 3 H, J = 6.6 Hz); high-resolution mass spectrum, calcd for $C_{12}H_{20}O_2$ m/e 196.1463, found m/e 196.1463.

***cis*-5-Methyl-2-cyclohexenyl pivalate (*cis*-1-OPiv)**, bp 106–110 °C (20 mm), was prepared from the corresponding alcohol[13] in a similar manner. Capillary GC showed this ester contained 0.5% trans isomer. This ester had the following: IR (neat) 3040 (m), 2940 (s), 2860 (s), 2820 (s), 1725 (s), 1480 (m), 1460 (m), 1280 (s), 1160 (s), 740 (m), 680 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.78–5.88 (ddt, 1 H, J = 1.8, 4.8, 10.1 Hz), 5.54–5.59 (br d, 1 H J = 10.3 Hz), 5.31–5.40 (m, 1 H), 1.10–2.20 (m, 14 H, t-Bu s at δ 1.19), 0.98 (d, 3 H, J = 6.6 Hz); high-resolution mass spectrum, calcd for $C_{12}H_{20}O_2$ m/e 196.1463, found m/e 196.1467.

***cis*-5-Methyl-2-cyclohexenyl *N*-phenylcarbamate (3)**, mp 91.5–92.5 °C (lit.[5] mp 91.5–92.5 °C), was prepared as described earlier[5] and purified by recrystallization from pentane. This material was shown to be >99.5% cis isomer by LAH reduction and capillary GC analysis of the resulting 5-methyl-2-cyclohexenol (94 ft, UCON LB-550X, 75 °C).

***cis*-3-*n*-Butyl-5-methylcyclohexene (*cis*-2)** was obtained in 44% isolated yield by alkylation of **3** with butyllithium by a three-step one-pot procedure (method D) reported previously.[5] After purification, *cis*-**2** had the following: bp 62–65 °C (10 mm); IR (neat) 3005 (m), 2950 (s), 2915 (s), 2860 (s), 1650 (w), 1460 (m), 1380 (w), 675 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.48–5.70 (m, 2 H), 1.90–2.20 (m, 2 H), 1.50–1.80 (m, 3 H), 1.20–1.40 (m, 6 H), 0.7–1.0 (m, 7 H); ^{13}C NMR (CDCl$_3$) δ 132.2, 126.3, 38.6, 36.2, 34.4, 29.2, 28.9, 24.7, 22.9, 22.5, 14.1. Attempts to analyze binary mixtures of *cis*- and *trans*-**2** by capillary GC were unsuccessful.

The configurational composition of the above alkylation product derived from **3** was determined by low-pressure catalytic hydrogenation (PtO$_2$) in acetic acid[14] to the saturated analogue 1-*n*-butyl-3-methylcyclohexane (**4**) and analysis of the latter by capillary GC (175 ft, squalane, 100 °C)[4] or (300 ft, QF-1, 110 °C). The cis/trans ratio for **4**, and thus that for **2** was 97/3. This confirms the syn stereospecificity of alkylation of **3** by the indicated procedure.[5]

***cis*-1-*n*-Butyl-3-methylcyclohexane (*cis*-4)**, derived from the above *cis*-**2**, had the followed: bp 72–74 °C (14 mm); IR (neat) 2940 (s), 2910 (s), 2840 (s), 1460 (m), 1378 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.08–1.80 (m, 14 H), 0.7–0.95 (m, 7 H), 0.4–0.6 (br q, 1 H, J = 12 Hz).

***trans*-3-*n*-Butyl-5-methylcyclohexene (*trans*-2)** was prepared in 83% isolated yield by alkylation of *cis*-5-methyl-2-cyclohexenyl acetate (*cis*-**2**-OAc) (99.5% cis isomer) with n-BuCu(CN)Li by a standard procedure reported earlier.[6] The trans/cis ratio of this product was shown to be 96.5/3.5 by hydrogenation to **4** followed by capillary GC analysis of the latter. Thus this confirms the anti stereospecificity for alkylation of *cis*-**2**-**OAc** with alkyl(cyano)cuprate.[6] After purification *trans*-**2** had the following: bp 64–67 °C (10 mm); IR (neat) 3010 (m), 2950 (s), 2920 (s), 2860 (s), 1460 (m), 1380 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.52–5.70 (m, 2 H), 1.96–2.16 (m, 2 H), 1.16–1.90 (m, 10 H), 0.8–1.00 (m, 6 H).

***trans*-1-*n*-Butyl-3-methylcyclohexane (*trans*-4)**, derived from the above *trans*-**2**, had the following: bp 66–69 °C (10 mm); IR (neat) 2950 (s), 2910 (s), 2860 (s), 1460 (m), 1380 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.00–1.80 (m, 16 H), 0.80–0.98 (m, 6 H).

(R)-(+)-α-Methyl-γ-phenylallyl alcohol (R-(+)-5-OH),[5] mp 58–60 °C, $[\alpha]^{30}_D$ 33.48° (c 5.39, CHCl$_3$) (96% ee),[5] was prepared as described earlier.[5,12]

(R)-(+)-α-Methyl-γ-phenylallyl pivalate (R-(+)-5-OPiv), bp 98 °C (0.5 mm), $[\alpha]^{25}_D$ 97.45° (c 4.92, CHCl$_3$), was obtained as an oil from the above (R)-(+)-5-OH and pivaloyl chloride in pyridine. The oil solidified on storage in a refrigerator. Spectral properties were undistinguishable from those of an authentic racemic sample.[1] The rotation of this product establishes that the absolute rotation for 5-OPiv is $[\alpha]^{25}_D$ 101.9° (c 5, CHCl$_3$).

(*dl*)-3-Methyl-1-phenylheptane (9). An authentic sample of this hydrocarbon was prepared as follows. 4-Phenyl-2-butanol (Aldrich) was converted to 4-phenyl-2-butyl p-toluenesulfonate in the usual manner. The tosylate derivative had the following: mp 49.5–50.5 °C; IR (KBr) 1490 (m), 1448 (m), 1380 (m), 1356 (s), 1342 (s), 1180 (s), 1165 (s), 1090 (m), 923 (s), 905 (s), 895 (s), 816 (s), 748 (s), 733 (s), 695 (s), 655 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.81 (d, 2 H, J = 7.7 H), 7.60–6.90 (m, 7 H), 4.66 (m, 1 H), 3.00–2.30 (m, 2 H), 2.46 (s, 3 H), 2.20–1.76 (m, 2 H), 1.31 (d, 3 H, J = 6.9 Hz) high-resolution mass spectrum calcd for $C_{17}H_{20}O_3S$ m/e 304.1128, found m/e 304.1134.

The above p-toluenesulfonate was cross coupled with n-Bu$_2$CuLi by a standard procedure,[15] and **9** was isolated as a clear mobile oil in 64% yield. After purification by vacuum distillation **9** had the following: bp 62 °C (0.6 mm); IR (neat) 3075 (w), 3050 (w), 3010 (m), 2940 (s), 2902 (s), 2850 (sh, s), 2840 (s), 1600 (w), 1490 (m), 1460 (sh, s), 1448 (s), 1372 (m), 1028 (w), 740 (s), 690 (s) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.16 (s, 5 H), 2.80–2.20 (m, 2 H), 2.00–1.02 (m, 9 H), 1.02–0.40 (m, 6 H); high-resolution mass spectrum calcd for $C_{14}H_{22}$ m/e 190.1716, found m/e 190.1722.

Alkylation of *trans*-5-Methyl-2-cyclohexenyl Pivalate (*trans*-1-OPiv) with *n*-BuMgBr Containing Cuprous Salts. In a typical experiment a flame-dried flask equipped with a magnetic stirrer and septum was charged with 6.5 mg (0.072 mmol) of CuCN and 682 mg (3.48 mmol) of *trans*-1-OPiv. After the flask was flushed with dry nitrogen, 26.5 mL of ether was added, and the reaction flask was placed in an ice bath. A solution of 6.96 mmol of n-BuMgBr in 8 mL of ether was added to the stirred solution, and stirring was continued for 1 h after which the reaction was quenched with 15 mL of saturated aqueous NH$_4$Cl. The resulting mixture was extracted several times with ether, and the

(13) Goering, H. L.; Nevit, T. D.; Silversmith, E. F. *J. Am. Chem. Soc.* **1955**, *77*, 4042. Goering, H. L.; Doi, J. T. *Ibid.* **1960**, *82*, 5850.

(14) Marshall, J. A.; Cohen, N.; Hochstetler, A. R. *J. Am. Chem. Soc.* **1966**, *88*, 3408.

(15) Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7777.

dried ($MgSO_4$) extract was concentrated by fractionation. Purification of the residue by vacuum distillation and thin-layer chromatography (silica gel, pentane) gave 0.4 g (83% yield) of alkylation product **2** which was shown to be 96.5% cis isomer by hydrogenation followed by GC analysis of the resulting saturated analogue **4**. The spectral properties of the alkylation product obtained in this experiment were indistinguishable from those for authentic *cis*-**2** described above.

The other experiments summarized below eq 1 were carried out in a similar manner. The alkylation product derived from *cis*-**1**-OPiv had the same spectral properties as an authentic sample of *trans*-**2**.

Alkylation of (*R*)-(+)-α-Methyl-γ-phenylallyl Pivalate (*R*-(+)-5-OPiv) with *n*-BuMgBr Containing 1 Mole % CuCN or CuCl. These procedures were the same as reported earlier for alkylation of racemic **5**-OPiv.[1]

The product obtained by alkylation with *n*-BuMgBr containing 1% CuCl was isolated in 96% yield, and the composition was determined by capillary GC (94 ft, UCON LB-550X, 130 °C). A portion of this product was converted to 2-methylhexanoic acid (**8**) by Lemieux oxidation using a procedure reported earlier for this same transformation.[12] A pure sample of **8** had $[\alpha]^{22}_D$ −20.09° (*c* 6.02, ether). From the absolute configuration and rotation for this compound,[12] it can be seen that this product had the *R* configuration and an ee of 92%. The spectral properties were the same as for an authentic sample of (*dl*)-**8**.[12]

A portion of the same alkylation product was reduced with diimide by a standard procedure published earlier for a similar transformation.[5] The reduction product was isolated in 91% yield and a homogeneous sample of 3-methyl-1-phenylheptane (**9**) was obtained by preparative GC (10 ft, UCON LB-550X on Chromosorb P, 130 °C). This material had the same spectral properties and capillary GC retention time as the authentic racemic sample described above. A homogeneous sample of **9** derived from the alkylation product had $[\alpha]^{25}_D$ −8.55° (*c* 3.58, *n*-hexane). This has the same configuration and ee as the (*R*)-(−)-**8** obtained from the same alkylation product. Thus (−)-**9** has the *R* configuration and the absolute rotation is $[\alpha]^{25}_D$ 9.3° (*n*-hexane). The results for alkylation of (*R*)-(+)-**5**-OPiv with *n*-BuMgBr containing 1 mol % CuCl are presented in Scheme I.

The product obtained by alkylation with *n*-BuMgBr containing 1% CuCN was isolated in "quantitative" yield. The composition was determined by capillary GC (94 ft, LB-550X, 130 °C) and (299 ft, QF-1, 130 °C). The latter column is effective for resolution of (*E*)- and (*Z*)-**7**.

Diimide reduction of this product by the procedure used earlier for this same transformation,[5] followed by purification by preparative GC (10 ft, UCON LB-550X on Chromosorb P, 130 °C), gave a homogeneous sample of **10**, $[\alpha]^{25}_D$ −5.40° (*c* 5.78, hexane). From the absolute configuration and rotation for this compound[5] it can be seen that this sample had the *R* configuration and an ee of 63%. The spectral properties and capillary GC retention time were the same as for an authentic sample.[5]

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Electronic Structure of Octavalene. Photoelectron Spectroscopic Investigations†

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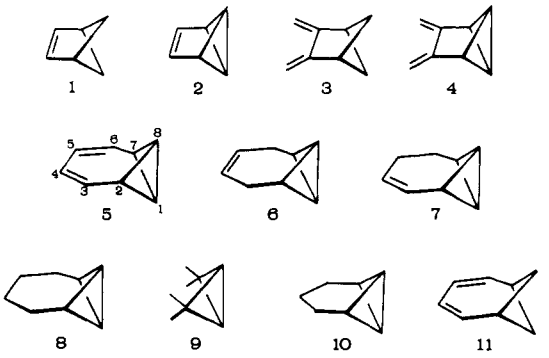
The He I photoelectron (PE) spectra of octavalene (**5**) as well as its hydrogenated products **6–8** have been investigated. The assignment given is based on an empirical comparison of **5–8** with related compounds, a ZDO model, and semiempirical and ab initio calculations. Within the ZDO model the interaction between the butadiene moiety and the bicyclobutane fragment of **5** is described by a resonance integral of −2.3 eV. The orbital sequence of **5** is found to be $2a_2$ ($\pi - \sigma$), $9a_1$ (σ), $3b_1$ ($\pi - \sigma$), $1a_2$ ($\sigma + \pi$), $2b_1$ ($\sigma + \pi$).

The comparison between bicyclo[2.1.1]hexene (**1**) and benzvalene (**2**) as well as 2,3-bis(methylene)bicyclo[2.1.1]hexane (**3**) and 3,4-bis(methylene)tricyclo[3.1.0.0^{2,6}]hexane (**4**) reveals a stronger interaction between the π fragment and the bicyclobutane moiety compared to the four-membered-ring fragment.[1] Using data from photoelectron (PE) spectroscopic investigations yields a resonance integral β of −1.9 eV for **1** and **3** and −2.3 eV for **2** and **4**.

The recent synthesis of octavalene (**5**)[2] and its hydrogenated congeners **6–8**[2c] allows us to explore the electronic structure of **5–8** and to check the above-mentioned interaction parameters.

In the following we will report on the He I PE data of **5–8**. In Figure 1 we show the PE spectra of **5–8** and in Table I we list the recorded vertical ionization energies, $I_{v,j}$.



PE Spectra. In the spectrum of **5** we encounter three bands below 11 eV. The first and third show a relatively steep onset while the second is more Gaussian like. In the PE spectrum of **6** we see two peaks below 12 eV. The

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