in an oil bath at 185–195 °C. Formaldehyde thus generated was passed into a round-bottomed flask (100 mL) containing ylide (1.8 g, 5.9 mmol) in dry acetonitrile (30 mL) cooled with ice/salt. The reaction mixture was allowed to reflux for 72 h. On removal of triphenylphosphine oxide in the usual manner, as described in the previous experiment, pyrazole **32e** was obtained (0.6 g, 75%). Compound **32e** was purified by column chromatography using silica gel and elution with a mixture of petroleum ether (85%) and ethyl acetate (15%). TLC, ^{1}H NMR, and GC indicated the presence of only one pyrazole. Pertinent ^{1}H NMR and ^{13}C NMR data are listed in Tables VIII and X.

Acknowledgment. The generous support of the National Institute of General Medical Sciences (Grant No. GM27620) is gratefully acknowledged. We also thank Dr. Roger Crecely of the University of Delaware for obtaining and discussing the ^{1}H, ^{31}P, and ^{13}C NMR spectra reported in this work with us. Purchase of the Brucker WM 250 was supported, in part, by a grant (GM 27616) from the National Institutes of Health.

Registry No. **12**, 2091-46-5; **13**, 104-55-2; **15**, 52372-79-9; **17**, 80890-24-0; **18**, 80878-43-9; **19a**, 123-11-5; **19b**, 104-87-0; **19c**, 100-52-7; **19d**, 104-88-1; **19e**, 105-07-7; **19f**, 529-20-4; **19g**, 66-77-3; **19h**, 66-99-9; **19i**, 555-16-8; **19j**, 552-89-6; **19k**, 50-00-0; **20a**, 80878-44-0; **20b**, 80878-45-1; **20c**, 80878-46-2; **20d**, 80878-47-3; **20e**, 80878-48-4; **20f**, 80878-49-5; **20g**, 80878-50-8; **20h**, 80878-51-9; **20i**, 80878-52-0; **20j**, 80907-72-8; **20k**, 80878-53-1; **23a**, 80878-54-2; **23b**, 80878-55-3; **23c**, 80878-56-4; **23d**, 80878-57-5; **23e**, 80878-58-6; **23f**, 80878-59-7; **23g**, 80878-60-0; **23h**, 80878-61-1; **23i**, 80878-62-2; **23j**, 80878-63-3; **23k**, 80878-64-4; **24a**, 80890-25-1; **24b**, 80878-65-5; **24c**, 80878-66-6; **24d**, 80878-67-7; **24e**, 80878-68-8; **24f**, 80878-69-9; **24g**, 80878-70-2; **24h**, 80878-71-3; **24i**, 80878-72-4; **24j**, 80878-73-5; **25**, 34387-64-9; **26**, 80878-75-7; **27**, 80890-26-2; **28**, 80878-76-8; **29a**, 80878-77-9; **29b**, 80878-78-0; **29c**, 80878-79-1; **29d**, 80878-80-4; 29e, 80878-81-5; **32a**, 80878-82-6; **32b**, 80878-83-7; **32c**, 80878-84-8; **32d**, 80878-85-9; **32e**, 80878-86-0; **33a**, 80878-87-1; **33b**, 80878-88-2; **33c**, 80878-89-3; **33d**, 80878-90-6.

Supplementary Material Available: The ^{1}H NMR parameters for azines **20** (Table IV), pyrazoles **23** (Table VI), pyrazoles **24** (Table VII), pyrazoles **32** (Table VIII), and pyrazoles **33** (Table IX) and the ^{13}C NMR parameters for azines **20** (Table V), pyrazoles **32** (Table X), and pyrazoles **33** (Table XI) (8 pages). Ordering information is given on any current masthead page.

Studies on the Pinacol Coupling Reaction

Bradford P. Mundy,* Ramanujan Srinivasa, Youseung Kim, and Thomas Dolph

Chemistry Department, Montana State University, Bozeman, Montana 59717

Ronald J. Warnet*[1]

Chemistry Department, Simpson College, Indianola, Iowa 50125

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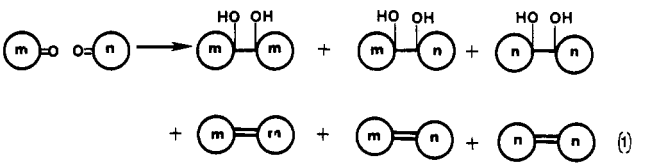
The mixed pinacol coupling reaction has been carefully analyzed. Although a trend toward statistical distribution of products can be found, it is observed that true statistical distributions are rarely observed. Ring-size and alkyl substituent effects are examined. A through-space heteroatom influence on coupling is noted. By use of (*R*)-(+)-3-methylcyclohexanone, a very specific effect of coupling conditions on product stereochemistry is observed.

Question of Statistical Distribution in a Mixed Coupling. There has been a consensus that the mixed pinacol coupling reaction results in a statistical distribution of products; however, this has never been subjected to critical examination. Since products resulting from mixed couplings might provide useful intermediates for subsequent pinacol rearrangements,[2] we embarked on a careful analysis of this reaction.

Cycloalkanones have been well-characterized as exhibiting differential reactivity of the carbonyl group as a function of ring size, best demonstrated with the careful study by Brown[3] on the borohydride reduction of this series. The potential for differential formation and/or reactivity of anion radicals from these cycloalkanones prompted us to examine this system. Equimolar amounts of two cyclic ketones in THF were added to the [Mg–Hg]/$TiCl_4$ reduction mixture developed by Corey (eq 1).[4]



(1)

After workup of the reactions, the products were examined by GLC to determine product ratios; peak areas of the chromatograms were integrated electronically. Each coupling reaction was independently performed three times. The raw data from the combined experiments are found in the Experimental Section.

For ease of evaluation, the results are presented in graphical format (Figure 1). Examination of the *normalized* pinacol ratios show that although there is a trend toward a statistical distribution of products, even with a liberal 10% error limit arbitrarily placed about the 25% and 50% statistical region, rarely do the experimental

(1) Visiting Professor of Chemistry, Montana State University, 1979–1980.

(2) The problems of regio- and stereocontrol of pinacol rearrangements will be discussed elsewhere.

(3) (a) Brown, H. C.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 22. (b) The reagent has also been used to examine steric effects in the methylcyclohexanones. Rickborn, B.; Wuesthoff, M. T. *J. Am. Chem. Soc.* **1970**, *92*, 6894.

(4) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260.

0022-3263/82/1947-1657$01.25/0

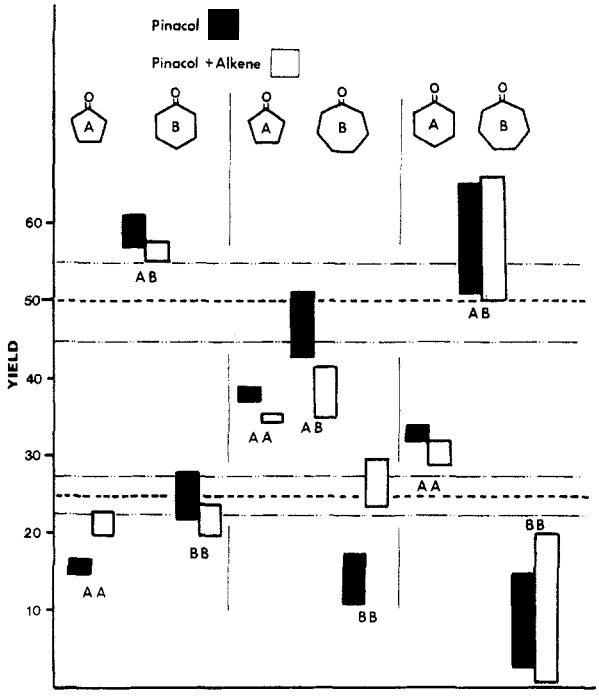


Figure 1. Ring size effect in pinacol coupling.

Table I. Self-Coupling of Methylcyclohexanones

methylcyclohexanone	% yield diol	alkene	starting matl
2-Me	8.6	1.8	88
3-Me	75.8	12.9	11.3
4-Me	64.6	1.7	33.7

results fall within the statistical regions.

The observation that alkene is formed in these reactions, coupled with McMurry's conclusions that alkene formation requires a pinacol precursor,[5] justifies a consideration of total coupling (alkene plus pinacol) for each ring size. These data are also presented in Figure 1. Inclusion of the alkene products tends toward making the data appear more statistical; however, even under these circumstances deviations are readily apparent.

We next embarked on a study of the extent to which steric effects would find expression in deviation from statistical coupling. In this study the ring size was held constant while steric congestion about the carbonyl was altered. The specific series examined included the mixed coupling of cyclohexanone with 2-, 3-, and 4-methylcyclohexanone, respectively. These experiments, also performed in triplicate, were carried out and analyzed in the same manner as the ring-size studies. Again, the raw data are found in the Experimental Section, and the results are summarized in Figure 2.

Not unexpected is the observation that 2-methylcyclohexanone experiences a substantial steric effect about the carbonyl. This is expressed not only in the tendency to avoid self-coupling but also in a poor disposition toward participation in mixed coupling. The 3-methyl isomer behaves as expected. The methyl group is sufficiently remote from the carbonyl to preclude any steric effect. However, we were quite surprised at the relative resistance of 4-methylcyclohexanone to undergo self-coupling.

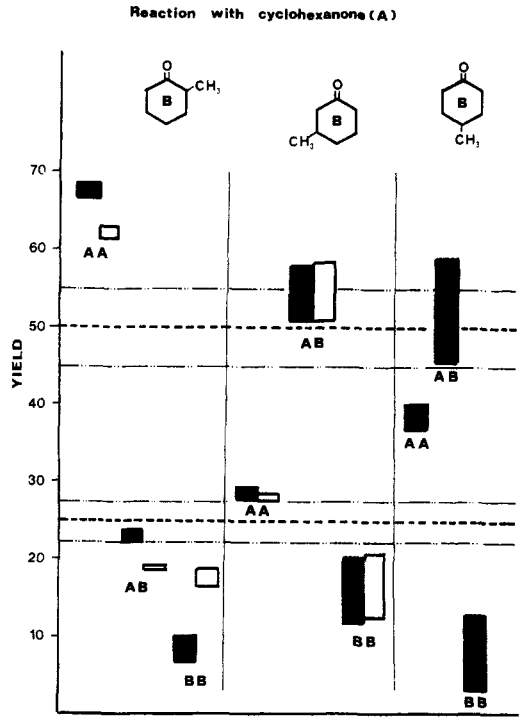
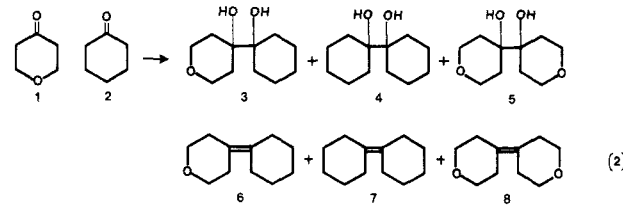


Figure 2. Competitive coupling of the methylcyclohexanones.

Dreiding models gave no useful hint to explain this observation.

The trends noted in these experiments can also find parallel expression in our specific attempts to self-couple the methylcyclohexanones (Table I). Here again, the resistance of the 4-methyl isomer to undergo coupling is quite apparent.

The most impressive case against the assumption of statistical coupling can be found in the attempt to prepare **3** (eq 2). Since the mixed product was needed for an



(2)

examination of heteroatom effects on pinacol rearrangement,[6] we followed the accepted procedure[4,5] of using a 4-fold excess of cyclohexanone to maximize the mixed coupling. Under these conditions, the statistical distribution [1:8:16 (5 + 8)/(3 + 6)/(4 + 7)] may be expected because (a) ring-size effects are minimized[7] and (b) there are no obvious steric effects. One observes from this reaction, however, yields as follows: **3**, 18.8%; **4**, 48.8%; **5**, 0%; **6**, 2.5%;[8] **7**, 26.6%; **8**, 2%;[8] about 1.5% of an unidentified material. Quite obviously, the amount of **3** (and **6**) formed from this reaction does not come close to that required if statistically driven.

Temperature Effects on the Coupling Reaction. As a consequence of one coupling experiment for which the temperature was not maintained at −10 °C, we undertook an analysis of temperature effects on the coupling reaction (Figure 3). From these results one can see a decrease in

(5) (a) McMurry, J. E.; Krespski, L. R. *J. Org. Chem.* **1976**, *41*, 3926. (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krespski, K. R. *Ibid.* **1978**, *43*, 3255. (c) Admittedly, McMurry's evidence is derived from a study of aromatic ketones, and at this juncture we have no direct evidence for dianions in our study.

(6) Manuscript submitted for publication.

(7) Mundy, B. P.; Srinivasa, R.; Otzenberger, R. D.; DeBernardis, A. R. *Tetrahedron Lett.* **1979**, 2673.

(8) These minor components are characterized only by relative GLC retention times and mass spectral molecular weights.

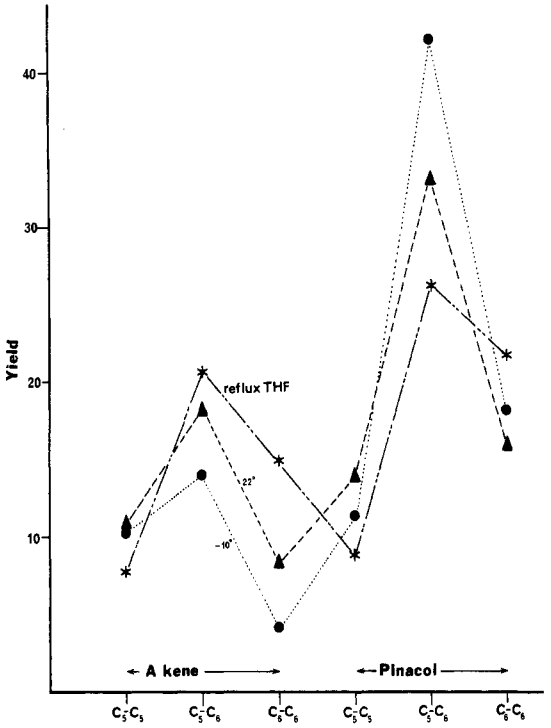


Figure 3. Temperature effects on the coupling reaction.

pinacol product with increasing temperature; however, at the same time the corresponding alkene product increases. This is again supportive of McMurry's arguments that pinacols serve as precursors to alkenes. Of greater interest; however, is the observation that the ring-size distribution does not appear to be influenced by temperature (C_5–C_5 products, 20.8 ± 3.9%; C_5–C_6 products, 51.5 ± 4.5%; C_6–C_6 products, 27.7 ± 7.6%). This might suggest that the coupling process is kinetically controlled, and for mixed coupling reactions the product distributions are determined by many of the factors which are seen to control other reactions, including ring strains, steric effects, and heteroatom participation. McMurry[9] has previously demonstrated that retro pinacol condensation does not occur for tertiary pinacols; thus there seems little reason to be concerned about equilibration taking place.

Effect of Reaction Conditions on the Coupling Reaction. The reductive coupling of carbonyl compounds to form pinacols can be carried out by using a variety of reductive conditions;[4] however, two procedures are most often used: the classical [Al–Hg] method[10] and the more recent [Mg–Hg]/$TiCl_4$ method.[4] The latter has been suggested as the method of choice for routine coupling, a consequence of the ease of reaction and the relatively good yields. Both Corey[4] and McMurry[5] have agreed that a reduced state of titanium is intimately involved in the coupling reaction; however, there is some question as to the exact oxidation state. There seems to be a tacit assumption that the titanium intermediates (of undefined nature) enhance the degree of coupling without affecting product composition. We now present evidence to unequivocally demonstrate that the pinacol product is *not* the same from the titanium-mediated reactions as from the [Al–Hg] reaction.

Our specific attention focused on **10**, the reported[11] pinacol derived from (*R*)-(+)-3-methylcyclohexanone (**9**).[12]

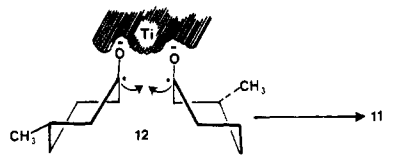
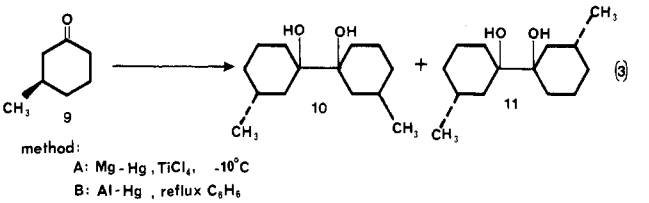


Figure 4. Titanium-mediated coupling of 3-methylcyclohexanone.

Because the reported preparation, using [Al–Hg], gave only a low yield of product, we undertook the reaction using the Corey procedure (eq 3, method A). A crude product



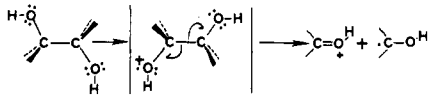
(78%) containing pinacol and alkene in the ration of 67:33, respectively, was readily purified by column chromatography (silica gel, ether–petroleum ether). The crystalline pinacol (mp 78.5–79 °C; *m/e* 226; $[\alpha]_D$ −4.3°) was homogeneous by GLC.

The optical rotation came as a surprise since the reported product derived from the [Al–Hg] reductive coupling (eq 3, method B)[11] had $[\alpha]_D$ +4.35°. In order to ensure that no unexpected epimerization of **1** had occurred, although admittedly a remote possibility, we cleaved the pinacol by the Malprade reaction.[13] The 3-methylcyclohexanone recovered, in quantitative yield, was shown by GLC and optical rotation to be identical with the starting reagent. This degradative procedure also assured us that we had, indeed, formed a pinacol from **9**, an observation further buttressed by mass spectrometry.[14] High-resolution proton NMR spectroscopy (250 MHz), combined with the requirement for optical activity, unambiguously fixed the structure of the pinacol. Only one methyl doublet (J = 6.1 Hz) at 0.88 ppm was observed, consistent with an equatorial methyl group. The only asymmetric pinacol which can be formulated to fit these data requires structure **11**.

At this juncture we were forced to repeat the [Al–Hg] reductive coupling of **9**. This was carried out according to the literature procedure,[11] giving a crude mixture (62%) of alkene and pinacol. Purification by the same procedures resulted in a homogeneous crystalline pinacol: mp 60–62 °C; $[\alpha]_D$ −4.4°.[11] The proton NMR spectrum of this pinacol gave two cleanly resolved methyl doublets (J = 6 Hz) centered at 0.85 and 1.10 ppm, consistent with an equatorial and axial orientation, respectively. These data are identical with those reported, supporting the assigned structure **10**.

Additional support for the structure assignment was obtained from the sulfite esters.[15] The diols (**10** and **11**) were individually mixed with thionyl chloride. From **10**

(9) McMurry, J. E.; Choy, W. *J. Org. Chem.* **1978**, *43*, 1800.
(10) A rapid survey of organic chemistry teaching manuals shows this to be the method of choice for carrying out the experiment at the undergraduate level.
(11) Munoz-Madrid, F.; Pasqual, J. *An. Ouim.*, **1978**, *74*, 1270.
(12) Obtained from Aldrich Chemical Co. and used as obtained; $[\alpha]^{24}$ +13.5°.
(13) Fieser, L; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 815.
(14) Major cleavage of this pinacol gave *m/e* 113, consistent with the cleavage shown below. We see this in all of the pinacols we have prepared.



(15) This method has been used to establish stereochemistry of pinacols: Reeve, W.; Davidsen, S. K. *J. Org. Chem.* **1979**, *44*, 3430.

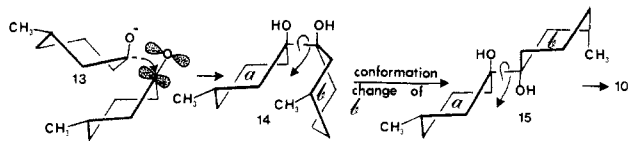


Figure 5. Nonradical coupling of 3-methylcyclohexanone.

was obtained a 1:1 mixture of two sulfite esters, expected from the requirement of both methyl groups being syn to the sulfinyl oxygen in one isomer and anti in the other isomer. For **11**, only one isomer is possible. The proton NMR spectra for the sulfites were not appreciably different from the diols, suggesting that the sulfinyl oxygen is sufficiently far from the protons not to cause a substantial influence.

Making use of the sensitive mechanistic probe afforded by the optically active ketone, we have unequivocally demonstrated that the two pinacol coupling procedures give different products from the same reactants, and this for the first time provides for a suggestion that the mechanistic interpretations may be significantly different. If we use Dreiding models and assume the traditional anion-radical intermediate,[16] the formation of **11** is readily apparent and readily allows for a Ti(IV) coordination of the two oxygen atoms, a possibility suggested by Corey (Figure 4).[4]

The formation of **10** is considerably more difficult to rationalize. There is a paucity of literature precedence for product composition depending upon reaction conditions; however, Ourisson[17] has demonstrated that different ratios of meso and *dl* products can be found under different reaction conditions, assuming the ketyl intermediate. Corey[4] has also presented evidence for *cis*- and *trans*-pinacols during intramolecular coupling reactions; however, these are also apparently consistent with an intermediate anion radical.

At this juncture we must make a few comments about the mechanistic interpretation of our observations. All the titanium-mediated reactions are readily rationalized by metal-bound ketyls. Even on the assumption that the role of metal in binding ketyls will change with each metal, the formation of **10** in the [Al–Hg] reaction is difficult to reconcile. Perhaps another explanation is required.

If we cannot account for **10** by an anion radical, what alternative is available? McMurry[5] has provided evidence for an intermediate dianion in reactions of aromatic ketones using the reduced titanium. Although we have no such ketone, reactions with aluminum are well-known to be two-electron-transfer reactions. Thus, a working hypothesis may include attack of a dianion from **9** on another molecule of **9**. The resulting intermediate would undergo immediate conformational reorganization to relieve a large 1,3-axial interaction. The resulting product would be **10** (Figure 5).

This mechanism seems more reasonable than the *only* alternative involving other anion radicals, which requires *a specific conformational change of only one of the two reacting partners*. We view this as highly improbably from three points of view: (1) if this were a facile interconversion, it should be seen in the titanium-mediated reaction; (2) there is no evidence that the conversion to the axial methyl should be an important contributor; (3) all evidence to date, including our study on mixed pinacol coupling, demonstrates that product mixtures *always* result from a mixed coupling reaction. We find only a single product.

At this juncture we conclude that the titanium-mediated products are rationalized by an anion-radical mechanism and that the classical methods may, in fact, involve different chemistry. We are now in the process of trying to more clearly identify the mechanism(s) of the many "classical" procedures and are also examining the olefin-forming reactions. Additional comments are pertinent. The different reaction products are most likely *not* a result of thermodynamic control for **11** and kinetic control for **10** since the experimental conditions (heat and long reaction periods) favoring a thermodynamic product are used for **10**. Additionally, we have subjected **11** to the method A conditions, at room temperature for 48 h, with very little conversion to alkene and no isomerization to **10**. Under conditions of Ti° ($TiCl_3$ and K)[5], **9** is converted totally to alkene in 2 h at room temperature. These observations may suggest unique chemistries of Ti° and Ti^{II}, and further research is in progress. To speak further against the question of thermodynamic isomerization, McMurry[9] has demonstrated that for teriary pinacols *no retro-pinacol condensations are observed.*

As a final test of this high selectivity observed for the two different reaction conditions, we tried to separate an artificial mixture of **10** and **11**. Under all GLC chromatographic methods used in these studies, **10** and **11** were not separable. Thus, if there were a reaction mixture, both products would have been collected together in the chromatographic separations. Since the NMR spectra do not show the presence of mixtures, we must conclude that the products from the two reactions are homogeneous.

One other observation can be made at this juncture. As a consequence of our finding that stereochemical features of products may vary with the method of accomplishing the pinacol (Mg–Hg/$TiCl_4$ vs. Al–Hg), we wanted to examine whether distribution trends might also be effected. We have repeated the pinacol coupling reaction of equimolar amounts of cyclohexanone and cyclopentanone using Al–Hg. In this method, deoxygenation to form alkenes is not observed, although some uncharacterized byproducts are found. However, from three independent examinations the pinacol distributions are as follows: C_5–C_5, 24.8 ± 2.6%; C_5–C_6, 47.5 ± 0.3%; C_6–C_6, 27.6 ± 2.8%. These data are within the range found for the titanium-mediated reaction.

In conclusion, we suggest that the long-held notion of a required statistical distribution does not hold up to experimental testing and that synthetic use of this process should not be based on these expectations. Additionally, it is evident that the method of coupling can dramatically influence the product composition. Much remains to be done.

Experimental Section

The coupling reactions were carried out in an identical manner, and a typical procedure is presented.

Dry THF (20 mL), distilled from $LiAlH_4$ prior to use, was added to 2.2 g of $HgCl_2$ and 5.9 g of Mg turnings. The mixture was stirred under N_2 for about 20 min, after which time most of the THF was withdrawn by syringe through a serum cap. The amalgam was washed three times with 20-mL portions of dry THF, maintaining the mixture under N_2. To the amalgam was added 150 mL of dry THF, and the reaction mixture was externally cooled to −10 °C. Titanium tetrachloride (13 mL) was added by syringe to the cooled solution, turning it yellow-green. The ketone (or 1:1 ketone mixture) totaling 80 mmol in 10 mL of solution added dropwise to the reaction mixture via syringe. The reaction was allowed to stir for 2 h, during which time it became dark

(16) Most discussions on the mechanism of the pinacol coupling reaction give as the reference: House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: New York, 1972; pp 167–169. There seems to be a paucity of studies directed toward testing this.

(17) Majerus, G.; Yax, E.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1967**, 4143.

Table II. Product Distribution (Percent) in the Ring Size Studies

expt	cyclo-alkanones	alkenes			pinacols		
		C_5-C_5	C_5-C_6	C_6-C_6	C_5-C_5	C_5-C_6	C_6-C_6
1	C_5 + C_6	10.2 ± 0.4	14.1 ± 1.6	4.1 ± 0.6	11.4 ± 0.3	42.0 ± 2.4	18.2 ± 3.8
		alkenes			pinacols		
expt	cyclo-alkanones	C_5-C_5	C_5-C_7	C_7-C_7	C_5-C_5	C_5-C_7	C_7-C_7
2	C_5 + C_7	8.0 ± 3.7	4.2 ± 2.9	16.7 ± 4.7	27.8 ± 4.3	33.9 ± 1.6	10.8 ± 3.7
		alkenes			pinacols		
expt	cyclo-alkanones	C_6-C_6	C_6-C_7	C_7-C_7	C_6-C_6	C_6-C_7	C_7-C_7
3	C_6 + C_7	1.8 ± 1.0	7.2 ± 5.5	4.8 ± 5.9	28.7 ± 6.5	48.8 ± 3.6	8.7 ± 6.4

Table III. Product Distribution in the Methylcyclohexanone Studies

expt[b,c]	olefin[a]			pinacol[a]		
	A-A	A-B	B-B	A-A	A-B	B-B
(1) 2-MeB + A	8.82 ± 0.16	0.83 ± 0.16	11.82 ± 0.29	59.13 ± 4.36	20.39 ± 1.27	8.01 ± 2.15
(2) 3-Me-B + A	2.05 ± 0.90	4.74 ± 1.18	1.75 ± 0.76	26.21 ± 2.33	49.61 ± 2.12	15.62 ± 5.54
(3) 4-Me-B + A				39.10 ± 7.51	51.97 ± 1.88	8.93 ± 5.85

[a] In percent. [b] A = cyclohexanone. [c] B = methylcyclohexanone.

purple in color. The temperature was allowed to rise to 0 °C during this period. The reaction mixture was quenched with 20 mL of saturated K_2CO_3, followed by 50 mL of ether. The reaction was filtered, and the filtrate was twice extracted with 50-mL portions of ether. The combined extracts were washed with saturated NaCl, dried over $MgSO_4$, and evaporated. Column chromatography was used to purify the products. We found that a silica gel column and combinations of petroleum ether–diethyl ether were suitable for isolating the products. Some mixtures required an alumina column. GLC analyses utilized either SE-30 or Carbowax as the liquid phase in the columns.

All of the pinacol products are readily characterized by a well-defined mass spectral fragmentation.[14] Details of these fragmentations will be presented elsewhere. Additionally, new compounds are characterized by the following physical and combustion data.

1-(1-Hydroxy-2-methylcyclohexyl)-2-methylcyclohexan-1-ol, mp 91.5 °C. Anal. Calcd for $C_{14}H_{22}O_2$: C, 74.28; H, 11.58. Found: C, 74.56; H, 11.29.

1-(1-Hydroxy-3-methylcyclohexyl)-3-methylcyclohexan-1-ol, mp 83.5–84.5 °C. Found: C, 74.49; H, 11.65.

1-(1-Hydroxy-4-methylcyclohexyl)-4-methylcyclohexan-1-ol, mp 117.5–118.5 °C. Found: C, 74.39; H, 11.55.

4-(Tetrahydropyranyl)cyclohexane-1,1-diol, mp 148–148.5 °C. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.70; H, 9.84.

Pinacols from the ring-size studies have been previously discussed.[7]

Pinacol Coupling of (*R*)-(+)-3-Methylcyclohexane. (a) [Al–Hg] Procedure To Prepare 10.[11] (*R*)-(+)-3-Methylcyclohexanone (5.0 g, 45 mmol) was added to a refluxing mixture containing Al (1.12 g, 47 mmol) and $HgCl_2$ (0.54 g, 2 mmol) in 10 mL of benzene. The mixture was refluxed for 1.5 h, at which time 10 mL of H_2O was added. After being stirred for a short while, the reaction mixture was filtered, and the filtrate was extracted with ether. The extracts were dried ($MgSO_4$), filtered, and evaporated to give a crude reaction product. Column chromatography gave the solid diol: mp 60–62 °C; [α] +4.40°; mass spectrum, *m/e* 226 (M^+); physical and spectral characteristics matched those reported.[11] Anal. Calcd for $C_{14}H_{22}O_2$: C, 74.28; H, 11.58. Found: C, 74.10; H, 11.58.

(b) [Mg–Hg]/$TiCl_4$ Procedure To Prepare 11. Magnesium (5.9 g, 243 mmol) and $HgCl_2$ (1.74 g, 6.4 mmol) were added to a flask containing dry THF and the contents then placed under a N_2 atmosphere. After cooling with a dry ice/isopropyl alcohol bath, $TiCl_4$ (13 mL, 22.4 g, 118 mmol) was slowly added via syringe to the stirred heterogeneous mixture. After the addition had been completed and the reaction subsided, the (*R*)-(+)-3-methylcyclohexanone (8.96 g, 80 mmol) in 10 mL of THF was added. The reaction mixture was allowed to stir for 2 h while slowly coming to room temperature. The reaction was quenched with 5 mL of saturated K_2CO_3 and filtered, and the filtrate was extracted with ether. The extracts were dried ($MgSO_4$), filtered, and evaporated to yield 7.0 g of crude product. Column chromatography (silica gel), eluting first with petroleum ether to remove alkene products and then with ether–petroleum ether, gave 2.1 g of pure diol: mp 78.5–79 °C; [α] −4.3°; mass spectrum, *m/e* 226 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 74.28; H, 11.58. Found: C, 74.10; H, 11.58.

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Registry No. 1, 29943-42-8; 2, 108-94-1; 3, 80879-18-1; 4, 2888-11-1; 5, 26170-26-3; 6, 80879-19-2; 7, 4233-18-5; 8, 80879-20-5; 9, 13368-65-5; 10, 70905-03-2; 11, 80925-00-4; 2,2′-dimethyl[1,1′-bicyclohexyl]-1,1′-diol, 80879-21-6; 3,3′-dimethyl[1,1′-bicyclohexyl]-1,1′-diol, 80925-01-5; 4,4′-dimethyl[1,1′-bicyclohexyl]-1,1′-diol, 68525-20-2; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 1-methyl-2-(2-methylcyclohexylidene)cyclohexane, 80879-22-7; 1-methyl-3-(3-methylcyclohexylidene)cyclohexane, 80879-23-8; 1-methyl-4-(4-methylcyclohexylidene)cyclohexane, 80879-24-9; cyclopentylidenecyclopentane, 16189-35-8; cyclopentylidenecyclohexane, 16189-54-1; cyclopentyldienecycloheptane, 80879-25-0; cycloheptylidenecycloheptane, 51175-34-9; cyclohexylidenecycloheptane, 51134-41-9; [1,1′-bicyclopentyl]-1,1′-diol, 5181-75-9; 1-(1-hydroxycyclopentyl)-cyclohexanol, 20170-99-4; 1-(1-hydroxycyclopentyl)cycloheptanol, 943-96-4; [1,1′-bicycloheptyl]-1,1′-diol, 27956-09-8; 1-(1-hydroxycyclohexyl)cycloheptanol, 73223-33-3; 1-methyl-2-cyclohexylidenecyclohexane, 80879-26-1; 1-methyl-3-cyclohexylidenecyclohexane, 80879-27-2; 2-methyl[1,1′-bicyclohexyl]-1,1′-diol, 80879-28-3; 3-methyl[1,1′-bicyclohexyl]-1,1′-diol, 80879-29-4; 4-methyl[1,1′-bicyclohexyl]-1,1′-diol, 80879-30-7.