Alkylation of Aldehyde (Arenesulfonyl)hydrazones with Trialkylboranes

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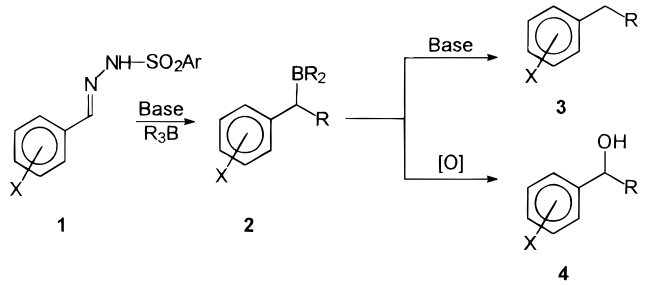
(Arenesulfonyl)hydrazone derivatives of aryl aldehydes are readily alkylated by trialkylboranes in the presence of base to generate new organoboranes that may be converted to the corresponding substituted alkanes or alcohols depending upon the reaction conditions chosen. Both tosyl- and trisylhydrazone derivatives can be utilized in the reaction, which tolerates a variety of functional groups, making it a versatile alternative to both the Grignard and Suzuki-coupling reactions.

Introduction

Alkylation of carbonyl compounds by organometallic reagents is one of the most useful reactions in synthetic organic chemistry. Typically, only active alkylmetals such as the organomagnesium,[1] organolithium,[2] or organozinc[3] reagents can be utilized to achieve this transformation. Trialkylboranes do not routinely alkylate carbonyl compounds, although a few exceptions are known.[4] The 1,2-addition of a trialkylborane to a carbonyl compound would be a valuable addition to organic methodology. The use of an organoborane reagent would eliminate many side reactions (enolization, condensation, etc.) that are associated with the strongly basic, traditional organometallic reagents[5] since organoboron reagents are not basic. In addition, most organoboranes are stable to protic solvents such as alcohols and water. Using organoboranes, a wide variety of functional groups[6] could then be incorporated early in the synthetic sequence. Finally, chiral organoborane reagents could be used to induce asymmetry in the product molecule, which is not easily accomplished with traditional organometallics.[7]

We recently reported the initial results of a study involving the alkylation of aryl aldehyde (arenesulfonyl)-hydrazones using trialkylboranes to produce the corresponding alkanes or alcohols in excellent yields upon workup (Scheme 1).[8] The oxidative reaction sequence is the equivalent of a 1,2-addition of a trialkylborane to a carbonyl. We now wish to report the results of a detailed study of this new reaction.

Scheme 1



Results and Discussion

Synthesis of Aryl Aldehyde (Arenesulfonyl)hydrazones 1. Two hydrazone derivatives were utilized in this study: tosylhydrazones **1** (Ar = Ts) and trisylhydrazones **1** (Ar = Tris; 2,4,6-triisopropylbenzenesulfonyl). Tosyl-[9] and trisylhydrazones[10] are stable, crystalline solids that were prepared according to literature procedures and purified by recrystallization from a minimum quantity of hot ethanol.

Synthesis of Arylalkanes 3. Hydrazone **1** is readily alkylated by trialkylboranes in the presence of base. The reaction generates a new trialkylborane **2** that can be protonolyzed to the corresponding alkane **3** or oxidized to the corresponding alcohol **4** (Scheme 1). It had been noted earlier that trialkylboranes capable of yielding stable carbanions after deboronation, e.g., **2**, are readily protonolyzed by base.[11] In this study, it was found that nucleophilic bases such as sodium hydroxide (NaOH) and tetrabutylammonium hydroxide (Bu_4NOH) produced excellent yields of **3** (Scheme 1). Heating the tosylhydrazone reactions to reflux in THF allowed them to proceed to completion in a reasonable time. Table 1 contains a summary of the reactions in which **3** was produced from **1** and tributylborane in the presence of these two bases. Bu_4NOH provided the highest yields of **3** in the shortest

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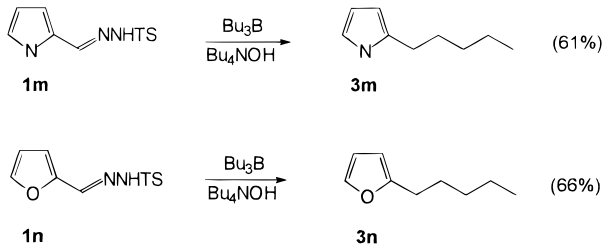
Table 1. Synthesis of Arylalkanes 3 from Tosylhydrazones 1

entry	tosylhydrazone	product	base	time (h)	% yield **3**[a]
1	**1a** (X = H)	**3a**	Bu_4NOH	1	80
2	**1a** (X = H)	**3a**	Bu_4NOH	1	78[b]
3	**1a** (X = H)	**3a**	NaOH	1	83
4	**1b** (X = 4-methyl)	**3b**	Bu_4NOH	1	90
5	**1b** (X = 4-methyl)	**3b**	NaOH	17	89
6	**1c** (X = 4-methoxy)	**3c**	Bu_4NOH	1.5	83
7	**1c** (X = 4-methoxy)	**3c**	NaOH	17	83
8	**1d** (X = 3-methoxy)	**3d**	Bu_4NOH	2.5	89
9	**1e** (X = 2-methoxy)	**3e**	Bu_4NOH	2	93
10	**1f** (X = 4-chloro)	**3f**	Bu_4NOH	1	94
11	**1f** (X = 4-chloro)	**3f**	NaOH	1.5	99
12	**1g** (X = 4-bromo)	**3g**	Bu_4NOH	1	94
13	**1g** (X = 4-bromo)	**3g**	NaOH	1	90
14	**1h** (X = 3-bromo)	**3h**	Bu_4NOH	1	89
15	**1h** (X = 3-bromo)	**3h**	NaOH	1	88
16	**1i** (X = 2-bromo)	**3i**	Bu_4NOH	1	92
17	**1i** (X = 2-bromo)	**3i**	NaOH	1	93
18	**1j** (X = 4-nitro)	**3j**	Bu_4NOH	1	98
19	**1j** (X = 4-nitro)	**3j**	NaOH	1	90
20	**1k** (X = 3-nitro)	**3k**	Bu_4NOH	1	91
21	**1k** (X = 3-nitro)	**3k**	NaOH	1	89
22	**1l** (X = 2,4,6-trimethyl)	**3l**	Bu_4NOH	24	91

[a] Isolated yields based on starting tosylhydrazones. [b] Tosylhydrazone prepared *in situ*.

Scheme 2



time, although the use of NaOH provides a simple alternative.

Excellent yields were obtained using either Bu_4NOH or NaOH with a variety of substituents present on the ring. The aryl aldehyde tosylhydrazones may be prepared beforehand or synthesized and used *in situ* without a significant decrease in the yield of the final product (Table 1, entries 1 and 2). Tosylhydrazones containing both electron-withdrawing and electron-donating substituents produced excellent yields of alkane, although reactants containing electron-donating groups required longer reaction times. Substitution at the *ortho* position did not significantly affect the overall reaction yields.

The reaction may also be extended to aromatic heterocycles. Both 2-pentylpyrrole and 2-pentylfuran were produced in good yields (Scheme 2). The slightly lower yields are presumably due to the increased electron density in the heterocyclic rings as compared to the substituted benzene derivatives. This makes formation of the anion (after deboronation) less favorable, which results in an incomplete hydrolysis under the reaction conditions.

The aryl aldehyde trisylhydrazones produce comparable yields of **3** under milder reaction conditions (Table 2). Trisylhydrazones with electron-withdrawing substituents are sufficiently reactive to produce the product alkane at room temperature. Trisylhydrazones with electron-donating substituents, however, must be heated to reflux to produce good yields of alkane.

At present, the reaction appears limited to aryl aldehyde derivatives. Preliminary experiments involving tosyl derivatives of aliphatic aldehydes have been unsuccessful, and only modest alkylation yields have been observed in reactions involving trisylhydrazones.[12]

Table 2. Synthesis of Arylalkanes 3 from Trisylhydrazones 1

entry	tosylhydrazone	product	time (h)	*T* (°C)	% yield **3**[a,b]
1	**1o** (X = H)	**3a**	1	reflux	98
2	**1p** (X = 4-methyl)	**3b**	1	reflux	88
3	**1q** (X = 4-methoxy)	**3c**	1.5	reflux	81
4	**1t** (X = 4-chloro)	**3f**	1	rt	93
5	**1u** (X = 4-bromo)	**3g**	1	rt	93
6	**1v** (X = 3-bromo)	**3h**	0.5	rt	96
7	**1w** (X = 2-bromo)	**3i**	0.5	rt	92
8	**1x** (X = 4-nitro)	**3j**	0.5	rt	95
9	**1y** (X = 3-nitro)	**3k**	0.5	rt	96

[a] Isolated yields based on starting trisylhydrazones. [b] Bu_4NOH used as base in all reactions!

Synthesis of Aryl Alcohols 4. Oxidation of intermediate **2** produces alcohol **4** if a non-nucleophilic base is utilized (Scheme 1). The use of a non-nucleophilic base minimizes the deboronation of **2** and subsequent protonolysis to **3**. Several bases were surveyed for use in this new reaction. Triethylamine, diisopropylethylamine, diethylamine, Proton Sponge (1,8-bis(dimethylamino)-naphthalene), and lutidine were examined. These hindered bases were not sufficiently basic to remove the sulfonamide proton from the tosylhydrazone in the initial step of the reaction.

The strong kinetic bases, butyllithium, lithium hexamethyldisilazide (LiHMDS), and sodium hydride, produced modest yields of the desired alcohol after oxidation. The chief drawback to their use is that they form tosylhydrazone anion salts that precipitate from solution, impeding further reaction with the trialkylborane. The hindered base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) produced a 43% yield of the desired alcohol product after 7 h at room temperature. Simply heating the reaction to reflux increased the yield of product to 73% in 1 h.

(12) The trisylhydrazone of heptanal was prepared and (without isolation) was added to a solution of tributylborane and DBU. Diazene **11** was isolated from the reaction mixture (after protonolysis) along with a 14% yield of the desired product, undecane.

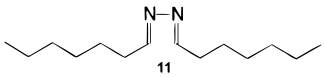


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Table 3. Synthesis of Aryl Alcohols 4 from Tosylhydrazones 1: Oxidation with Sodium Perborate

entry	tosylhydrazone	products	time (h)	% yield **4**[a]	% yield **3**[a]
1	**1a** (X = H)	**4a/3a**	0.5	73	15[b]
2	**1b** (X = 4-methyl)	**4b/3b**	1.5	83	5[b]
3	**1c** (X = 4-methoxy)	**4c/3c**	3	71	8[b]
4	**1d** (X = 3-methoxy)	**4d/3d**	1.5	76	15
5	**1e** (X = 2-methoxy)	**4e/3e**	1.5	86	14
6	**1g** (X = 4-bromo)	**4g/3g**	1	30	70
7	**1j** (X = 4-nitro)	**4j/3j**	1	0	87
8	**1l** (X = 2,4,6-trimethyl)	**4l/3l**	1	90	0

[a] Isolated yield based on tosylhydrazone. [b] GC yield.

Thus, DBU is sufficiently basic to produce the tosylhydrazone anion necessary for reaction with the trialkylborane. It is also non-nucleophilic and does not protonolyze the intermediate organoborane **2**. Consequently, DBU was chosen as the standard base for this study.

The alcohol synthesis involves, in the last step, the oxidation of intermediate **2** to alcohol **4** (Scheme 1). Compound **2**, a benzylic organoborane, is particularly susceptible to protonolysis to form **3**. Consequently, the use of the classic sodium hydroxide−hydrogen peroxide oxidation procedure must be avoided to maximize the yield of the desired alcohol.[13]

Sodium perborate ($NaBO_3 \cdot 4H_2O$) is a stable, easily handled, solid oxidant that has been shown to be an efficient oxidizing agent for trialkylboranes.[14] Perborate oxidations proceed at room temperature under conditions less stringent than the classical peroxide procedure. Use of this oxidant produced the desired alcohol, **4**, in good yields from most tosylhydrazone substrates (Table 3). Minor amounts of alkane **3** are produced as a byproduct since water is added along with the sodium perborate, and some hydrolysis occurs.

Both the methoxy- and methyl-substituted tosylhydrazones produce good yields of alcohol **4**. The results from reactions utilizing the isomeric methoxy derivatives (Table 3, entries 3−5) demonstrate that the reaction is insensitive to substituent regiochemistry. The hindered 2,4,6-trimethyl derivative (Table 3, entry 8), prepared from mesitaldehyde, produced an excellent yield of alcohol **4l**, which suggests that the reaction is also insensitive to steric effects in the tosylhydrazone. The 4-bromobenzaldehyde (**1g**) and 4-nitrobenzaldehyde (**1j**) tosylhydrazones produced the corresponding alkanes as the major products. Electron-withdrawing substituents in the *para* position presumably stabilize the benzylic anion leading to the formation of alkane (Table 3, entries 6 and 7). Thus, less basic oxidants were investigated.

Peracetic acid has been used to successfully oxidize water-sensitive organoboranes.[15] The use of peracetic acid increased the yield of **4** dramatically (Table 4). For example, the use of peracetic acid reversed the result obtained with sodium perborate for the 4-bromo derivative (Table 4, entry 3, versus Table 3, entry 6). Several substrates bearing electron-withdrawing groups were oxidized with peracetic acid, and most gave excellent yields of alcohol **4** with the remainder of product being alkane **3**. The results obtained utilizing the three bromo

Table 4. Synthesis of Aryl Alcohols 4 from Tosylhydrazones 1: Oxidation with Peracetic Acid

entry	Tosylhydrazone	Products	Time (h)	% Yield **4**[a]	% Yield **3**[a]
1	**1a** (X = H)	**4a/3a**	0.5	74	17
2	**1f** (X = 4-chloro)	**4f/3f**	0.5	80	15[b]
3	**1g** (X = 4-bromo)	**4g/3g**	1	80	17
4	**1h** (X = 3-bromo)	**4h/3h**	1	78	18
5	**1i** (X = 2-bromo)	**4i/3i**	1	80	17[b]
6	**1j** (X = 4-nitro)	**4j/3j**	1	0	84
7	**1k** (X = 3-nitro)	**4k/3k**	1	62	23

[a] Isolated yield based on starting tosylhydrazone. [b] GC yield.

Table 5. Synthesis of Aryl Alcohols 4 from Tosylhydrazones 1: Oxidation with TMANO

entry	tosylhydrazone	products	time (h)	% yield **4**[a]	% yield **3**[a]
1	**1a** (X = H)	**4a/3a**	0.5	83	
2	**1j** (X = 4-nitro)	**4j/3j**	1	0	84
3	**1k** (X = 3-nitro)	**4k/3k**	1	64	24

[a] Isolated yield based on tosylhydrazone.

derivatives (Table 4, entries 3-5) demonstrate, again, that the regiochemistry of the substituent has little effect on the yield of the reaction.

The 3-nitro derivative (Table 4, entry 7) produced a relatively low yield of alcohol **4k** compared to the other entries, presumably due to the electron-withdrawing properties of the nitro group. In fact, when the nitro group was *para* to the original carbonyl group (Table 4, entry 6), only the alkane product was produced. Both oxidizing procedures ($NaBO_3 \cdot 4H_2O$ and peracetic acid) produced only alkane **3j** from the 4-nitro substrate. Use of an anhydrous oxidant, trimethylamine *N*-oxide (TMANO),[16] also resulted in exclusive production of alkane **3j** (Table 5). Apparently, the 4-nitro group stabilizes the incipient benzylic anion involved in the protonolysis of the intermediate organoborane to such an extent that it becomes the primary reaction pathway. Use of the anhydrous TMANO oxidation also did not enhance the yield of alcohol **4k** obtained from the 3-nitro derivative **1k** (Table 5, entry 3). It did, however, increase the yield of alcohol **4a** produced from benzaldehyde tosylhydrazone, **1a** (Table 5, entry 1).

The aryl aldehyde trisylhydrazones were then investigated as substrates for the alcohol synthesis. These derivatives produced alcohol **4** in excellent yield and proceeded under very mild conditions. Whereas the tosyl derivatives required heating to reflux in THF, the trisyl derivatives reacted at room temperature to give comparable or enhanced yields of product (Table 6).

The standard oxidizing procedures were also utilized for the trisylhydrazone reactions. Both sodium perborate (Table 6, entries 1−5 and 9) and peracetic acid (Table 6, entries 6−8) were used as oxidants. Good yields of alcohol **4** were obtained when either electron-withdrawing or electron-donating groups were present in the trisylhydrazone starting materials. The hindered 2,4,6-trimethyl derivative **1z** also produced an excellent yield of alcohol **4l**.

An anomalous result was obtained when bromine was present in the *ortho* position (Table 6, entry 8). Instead of alcohol **4i**, a good yield of the corresponding alkane **3i** was isolated. It was initially hypothesized that the increased basicity of the trisyl anion, together with the *ortho* effect of the electron-withdrawing substituent,

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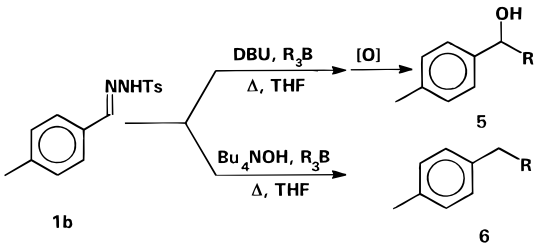
Table 6. Synthesis of Aryl Alcohols 4 from Trisylhydrazones 1

entry	trisylhydrazone	product	time (h)	% yield **4**[a]
1	**1o** (X = H)	**4a**	2	90[b]
2	**1p** (X = 4-methyl)	**4b**	2	87[b]
3	**1q** (X = 4-methoxy)	**4c**	3	80[b]
4	**1r** (X = 3-methoxy)	**4d**	1	76[b]
5	**1s** (X = 2-methoxy)	**4e**	1	88[b]
6	**1u** (X = 4-bromo)	**4g**	1	86[c]
7	**1v** (X = 3-bromo)	**4h**	1	83[c]
8	**1w** (X = 2-bromo)	**4i**	1	0[c,d]
9	**1z** (X = 2,4,6-trimethyl)	**4l**	1	91[b]

[a] Isolated yield based on starting hydrazone. [b] Sodium perborate used as oxidant. [c] Peracetic acid was used as oxidant. [d] 89% yield of alkane product isolated. [e] 82% yield of alkane product isolated.

Table 7. Reaction of *p*-Tolualdehyde Tosylhydrazone with Various Trialkylboranes



entry	R	products	**5**[a,b] (%)	**6**[a,c] (%)
1	$-CH_2(CH_2)_3CH_2Cl$	**5aa/6aa**	75	91[d]
2	$-CH_2(CH_2)_3CH_2CN$	**5bb/6bb**	72	98
3	$-CH_2(CH_2)_9COOCH_3$	**5cc/6cc**	75	89
4	−Chx[e]	**5dd/6dd**	68	71
5	$-CH(CH_3)CH_2CH_3$	**5ee/6ee**	51	62
6	−Ph[f]	**5ff/6ff**		80

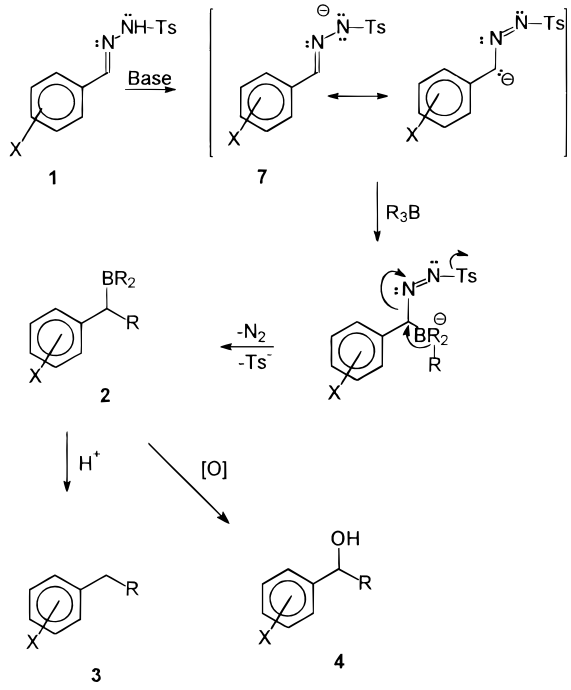
[a] Isolated yields. [b] Oxidized using sodium perborate. [c] Bu_4NOH used as the base. [d] Two equivalents of Bu_4NOH. [e] Chx = cyclohexyl. [f] From triphenylboron.

contributed to the production of alkane product. However, when this concept was tested by preparing the intermediate organoborane that would be formed from the reaction of 2-bromobenzaldehyde tosylhydrazone with base and then treating it with the trisyl anion, none of alkane **3i** was observed. Current research is directed at clarifying these unusual results.

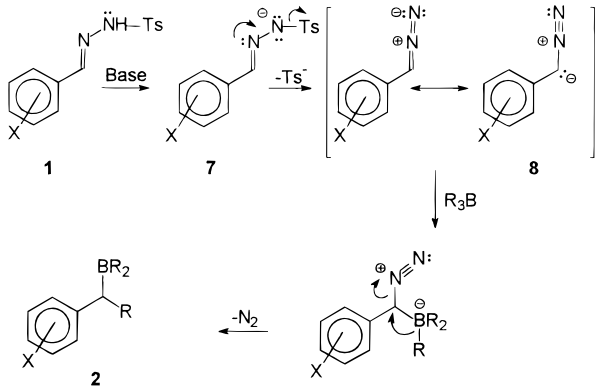
Functionalized Organoboranes. Organoboranes have been particularly useful in organic synthesis because of their exceptional tolerance of a wide variety of functional groups. An advantage of this new reaction is that functionalized alkyl groups can thus be incorporated into the alcohol or alkane product. As noted previously, this is difficult to achieve using traditional organometallic reagents. Table 7 contains examples of functionalized organoboranes that were reacted with *p*-tolualdehyde tosylhydrazone, **1b**, and the yields of the respective product alkanes and alcohols obtained. Entries 1−3 (Table 7) demonstrate that halo, cyano, and ester groups are readily tolerated using this methodology and good yields of either the corresponding alcohol or alkane are obtained. Entries 4 and 5 (Table 7) reveal that secondary alkyl groups may also be utilized. Finally, entry 6 (Table 7) shows that a phenyl group can be transferred. In this case, production of the corresponding alcohol is difficult to achieve due to the ready protonolysis of the intermediate organoborane with two electronegative aromatic groups attached to the benzylic carbon.

Mechanism of the Reaction. There are two possible mechanistic courses for the new reaction. In the first, the anion mechanism, removal of a proton from the

Scheme 3



Scheme 4



starting tosylhydrazone would generate an anion (**7**, Scheme 3). The trialkylborane would then react with this anion to form an electron-rich organoborane complex that would spontaneously undergo a 1,2-boratropic shift,[17] expelling nitrogen and the *p*-toluenesulfinate anion, to produce the new organoborane **2**. The new benzylic borane would then be hydrolyzed to the corresponding alkane **3** or oxidized to alcohol **4**. Alternatively, the reaction could proceed via a diazo mechanism (Scheme 4). Removal of a proton from the aryl aldehyde tosylhydrazone would generate the anion, which could then decompose to the intermediate diazo compound, **8**, prior to reacting with the trialkylborane. The borate complex, once formed, would undergo a spontaneous 1,2-boratropic shift, expelling nitrogen, to generate trialkylborane **2**. Reactions of α-diazocarbonyl compounds with trialkylboranes are known.[18] The difficulty in elucidating which mechanism is operative lies in the fact that they differ only in the timing of the tosyl group loss.

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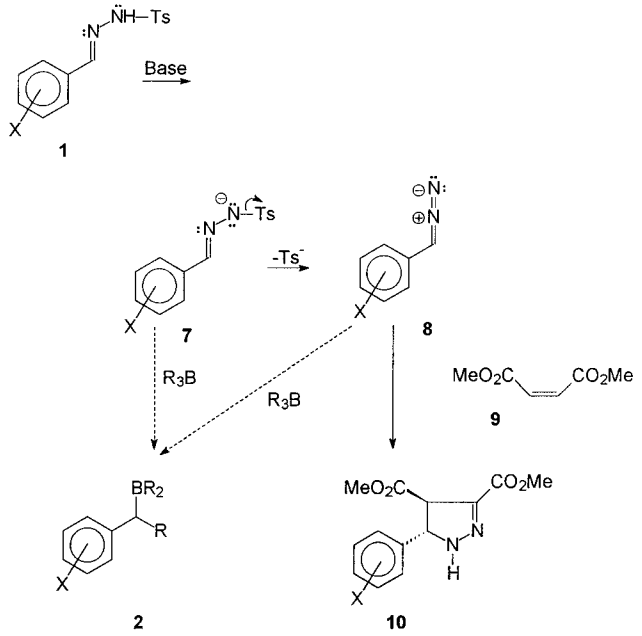
Scheme 5



Tosylhydrazones have been used to generate diazo compounds,[19] and the generation of an aryl diazo compound, such as that shown in Scheme 4, is possible under the conditions employed in this new reaction. When *p*-tolualdehyde tosylhydrazone was treated with DBU in the absence of an organoborane under the standard reaction conditions, a deep red color formed that can be attributed to the formation of a diazo compound. In fact, when pentane extracts of this reaction mixture were examined by IR, a sharp band at 2050 cm^{-1} was noted. The characteristic IR band of aryl diazo compounds has been reported to be in the range 2020−2060 cm^{-1}.[19c] The reaction, however, does not go to completion, and as evidenced by TLC, starting tosylhydrazone was still present after the typical reaction period of 1 h. Recovery of the starting material was verified by flash chromatography, which resulted in a 29% recovery of *p*-tolualdehyde tosylhydrazone. *p*-Toluenesulfonohydrazide was also detected, which indicates that decomposition of the starting hydrazone also took place.

Dimethyl maleate was then used to probe the reaction mechanism. Dimethyl maleate reacts with aryl diazo compounds via a 1,3-dipolar cycloaddition to generate *trans*-5-aryl-4,5-dihydro-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl esters (**10**, Scheme 5).[20] Reaction of *p*-tolualdehyde tosylhydrazone, **1b**, with dimethyl maleate and DBU in the absence of trialkylborane in refluxing THF, produced a 76% isolated yield of **10b**. When the reaction was run in the presence of trialkylborane (Scheme 5), an 80% isolated yield of alcohol (trialkylborane reaction) was produced after oxidation and none of pyrazoline **10b** was detected. In an attempt to enhance the rate of the maleate reaction, it was repeated but modified such that the solution containing **1b**, the borane, and dimethyl maleate was heated to reflux prior to the addition of base. Once again, a 77% yield of alcohol was produced. These results suggest that either the reaction proceeds via the anion mechanism or the reaction of the trialkylborane with the diazo intermediate is more efficient than the cycloaddition with dimethyl maleate.

The reaction of trialkylboranes with diazo compound **8** was then investigated. Compound **8a** (X = H) was prepared in 90% yield from benzaldehyde trisylhydrazone.[10b] The diazo compound was then reacted with tributylborane under a variety of conditions. In the first series of experiments, a solution of tributylborane in THF was added directly to **8a**. Vigorous gas evolution was observed, and several products were formed but little of the desired alcohol **4a** was obtained after oxidation. Then, a solution of **8a** in THF was added dropwise to a solution of tributylborane in THF; in this case, 37% of the alcohol product was isolated after oxidation. When the dropwise addition reaction was conducted in the presence of DBU, 55% of **4a** was isolated after oxidation. This is much lower than the 90% yield typically produced under the normal trisylhydrazone reaction conditions. A 2-fold excess of **8a** was necessary to produce 93% of the desired product **4a**. It is therefore possible to obtain the desired alkylation reaction via reaction of the diazo intermediate with tributylborane, but a 2-fold excess is necessary to obtain a yield comparable to that observed in the *in-situ* reaction.

Benzaldehyde trisylhydrazone was then mixed with DBU in THF to determine if the diazo compound is produced under the normal reaction conditions. After 2 h at room temperature, very little starting material was consumed and a small amount of the diazo compound formed. To eliminate the possibility that tributylborane, a Lewis acid, catalyzes the formation of the diazo intermediate, tribromoborane was added to a mixture of benzaldehyde trisylhydrazone and DBU. Tribromoborane had no effect on the formation of the diazo compound, and disappearance of the starting material was not observed.

Both the tosyl and trisyl reactions were monitored by ^{11}B NMR. Immediate formation of an intermediate was detected at room temperature in both cases upon addition of DBU to the reaction mixture. This was evidenced by an upfield shift of the ^{11}B resonance. In the trisylhydrazone reaction mixture, the boron resonance shifted from 85 to 18 ppm, while in the tosylhydrazone reactions, a shift to 37 ppm was observed. The borate intermediate then disappeared, and a new resonance appeared at 8 ppm in both reactions. The reaction was repeated using the diazo compound. **8a** was slowly added to a solution of tributylborane and DBU in THF at −78 °C. ^{11}B-NMR analysis revealed a resonance at −4 ppm. When the reaction mixture was allowed to come to rt, a new resonance was observed at 1 ppm. These results differ from those obtained in the hydrazone reactions and suggest that the hydrazone reactions do not proceed via the diazo mechanism.

Conclusions. The development of a new alkylation reaction that is the synthetic equivalent of the 1,2-addition of a trialkylborane to a carbonyl compound has been achieved. Both aryl aldehyde tosylhydrazones and trisylhydrazones are readily alkylated with trialkylboranes in the presence of base to produce the corresponding substituted arylalkanes or alcohols. Several functional groups may be present in either the hydrazone or the trialkylborane. The trisylhydrazones react more readily than the corresponding tosylhydrazones, producing either the alkane or alcohol products in excellent

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yields at room temperature. The reaction thus provides a useful alternative to both the Grignard and transition-metal-catalyzed coupling reactions such as the Suzuki reaction.[21]

Experimental Section

All melting points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

All glassware, syringes, and needles were dried in an oven heated to 250 °C for at least 12 h and cooled under argon prior to use. All solvents were dried and distilled prior to use.[22] Reactions were magnetically stirred and monitored by TLC. Products were purified by flash chromatography using 230−400 mesh ASTM 60 Å silica gel.[23]

Tributylborane, triphenylborane, and *p*-toluenesulfonohydrazide were purchased from Aldrich Chemical Co. and used without further purification. 2,4,6-Triisopropylbenzenesulfonohydrazide was prepared from 2,4,6-triisopropylbenzenesulfonyl chloride according to the literature procedure.[10a] 5-Chloro-1-pentene (Fairfield Chemical Co.), 5-hexenitrile (Acros Chemical Co.), and methyl 10-undecenoate (Eastman Chemical Co.) were hydroborated according to published procedures to generate the functionalized trialkylboranes listed in Table 5.[24−26]

General Procedure for the Synthesis of Aryl Aldehyde Tosylhydrazones. To a solution of *p*-toluenesulfonohydrazide (5.62 g, 30.2 mmol) in absolute ethanol (17 mL) was added the aldehyde (26.6 mmol). The reaction mixture was stirred and heated to reflux for 10 min. The mixture was cooled, and the precipitated product was collected and recrystallized from hot ethanol.

The yields and melting points of the tosylhydrazone products are presented in Table 8 (Supporting Information). The physical and spectral properties of previously reported compounds were in accord with literature values and are summarized in Table 9 (Supporting Information). The physical data from newly prepared derivatives are presented below.

3-Methoxybenzaldehyde tosylhydrazone (1d): ^{1}H-NMR (acetone-d_6) δ 10.14 (s, 1H), 7.95 (s, 1H), 7.85 (d, 2H, J = 8.2 Hz), 7.37 (d, 2H, J = 8.2 Hz), 7.28 (t, 1H, J = 7.8 Hz), 7.20−7.13 (m, 2H), 6.96−6.90 (m, 1H), 3.78 (s, 3H), 2.36 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 159.67, 147.87, 144.22, 135.17, 134.53, 129.64, 129.54, 127.86, 120.43, 116.64, 111.40, 55.26, 21.50. Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20. Found: C, 59.26; H, 5.34; N, 9.25.

2-Pyrrolecarboxaldehyde tosylhydrazone (1m): ^{1}H-NMR (DMSO-d_6) δ 11.22 (br s, 1H), 7.77 (d, 2H, J = 8.2 Hz), 7.72 (s, 1H), 7.36 (d, 2H, J = 8.2 Hz), 6.83 (d, 1H, = 1.1 Hz), 6.33 (s, 1H), 6.05 (m, 1H), 2.34 (s, 3H); ^{13}C-NMR (DMSO-d_6) δ 142.99, 140.26, 136.48, 129.41, 127.23, 126.53, 122.08, 112.76, 108.99, 20.93. Anal. Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.74; H, 4.98; N, 15.96. Found: C, 54.63; H, 5.02; N, 15.93.

2-Furaldehyde tosylhydrazone (1n): ^{1}H-NMR (DMSO-d_6) δ 11.42, (s, 1H), 7.80−7.70 (m, 4H), 7.38 (d, 2H, J = 8.1 Hz), 6.79 (d, 1H, J = 3.3 Hz), 6.54 (m, 1H), 2.34 (s, 3H); ^{13}C-NMR (DMSO-d_6) δ 148.55, 145.00, 143.43, 136.88, 136.09, 129.65, 127.12, 113.80, 111.95, 20.94. Anal. Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.53; H, 4.58; N, 10.60. Found: C, 54.66; H, 4.64; N, 10.68.

General Procedure for Synthesis of Aryl Aldehyde Trisylhydrazones. To a stirred solution of 2,4,6-triisopropylbenzenesulfonohydrazide (3.28 g, 11.0 mmol) in anhydrous methanol (45 mL) was added the aldehyde (9.97 mmol). A solid immediately precipitated, and the mixture was stirred at room temperature for 1 h. The mixture was placed in a refrigerator overnight, and the resulting solid was collected by vacuum filtration and washed with 3 × 5 mL of cold methanol. The products were recrystallized from hot ethanol.

The physical and spectral properties of previously reported compounds were in accord with literature values. The physical data from newly prepared derivatives are presented below.

4-Methylbenzaldehyde trisylhydrazone (1p): ^{1}H-NMR (DMSO-d_6) δ 11.61 (s, 1H), 7.89 (s, 1H), 7.41 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 8.0 Hz), 4.23 (sept, 2H, J = 6.7 Hz), 2.88 (sept, 1H, J = 6.7 Hz), 2.27 (s, 3H), 1.21 (d, 12H, J = 6.7 Hz), 1.17 (d, 6H, J = 7.1 Hz); ^{13}C-NMR (DMSO-d_6) δ 152.58, 150.37, 144.94, 139.60, 132.56, 131.15, 129.26, 126.47, 123.53, 33.29, 29.14, 24.67, 23.33, 20.86. Anal. Calcd for $C_{23}H_{32}N_2O_2S$: C, 68.96; H, 8.05; N, 6.99. Found: C, 68.93; H, 8.06; N, 7.04.

4-Methoxybenzaldehyde trisylhydrazone (1q): ^{1}H-NMR (DMSO-d_6) δ 11.49 (s, 1H), 7.88 (s, 1H), 7.47 (d, 2H, J = 8.6 Hz), 7.22 (s, 2H), 6.92 (d, 2H, J = 8.6 Hz), 4.24 (sept, 2H, J = 6.6 Hz), 3.74 (s, 3H), 2.88 (sept, 1H, J = 6.8 Hz), 1.21 (d, 12H, J = 6.7 Hz), 1.16 (d, 6H, J = 6.9 Hz); ^{13}C-NMR (DMSO-d_6) δ 160.58, 152.53, 150.38, 144.88, 132.61, 128.06, 126.45, 123.49, 114.17, 55.22, 33.30, 29.14, 24.68, 23.32. Anal. Calcd for $C_{23}H_{32}N_2O_3S$: C, 66.31; H, 7.74; N, 6.72. Found: C, 66.49; H, 7.67; N, 6.95.

3-Methoxybenzaldehyde trisylhydrazone (1r): ^{1}H-NMR (DMSO-d_6) δ 11.75 (s, 1H), 7.91 (s, 1H), 7.31−7.23 (m overlapping s, 3H), 7.10−7.08 (m, 2H), 6.94−6.90 (m, 1H), 4.26 (sept, 2H, J = 6.7 Hz), 3.73 (s, 3H), 2.90 (sept, 1H, J = 6.8 Hz), 1.24 (d, 12H, J = 6.7 Hz), 1.20 (d, 6H, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 159.73, 153.44, 151.29, 146.12, 134.70, 131.20, 129.49, 123.82, 120.58, 116.96, 110.71, 55.20, 34.13, 29.96, 24.79, 23.47. Anal. Calcd for $C_{23}H_{32}N_2O_3S$: C, 66.31; H, 7.74; N, 6.72. Found: C, 66.24; H, 7.78; N, 6.72.

2-Methoxybenzaldehyde trisylhydrazone (1s): ^{1}H-NMR (DMSO-d_6) δ 11.61 (s, 1H), 8.26 (s, 1H), 7.58−7.55 (m, 1H), 7.35−7.29 (m, 1H), 7.22 (s, 2H), 7.03−6.86 (m, 1H), 4.23 (sept, 2H, J = 6.7 Hz), 3.78 (s, 3H), 2.88 (sept, 1H, J = 6.8 Hz), 1.20 (d, 12H, J = 6.8 Hz), 1.17 (d, 6H, J = 6.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 157.76, 153.27, 151.36, 142.38, 131.41, 126.43, 123.79, 121.88, 120.58, 110.93, 55.15, 30.03, 24.90, 24.82, 23.55. Anal. Calcd for $C_{23}H_{32}N_2O_3S$: C, 66.31; H, 7.74; N, 6.72. Found: C, 66.17; H, 7.69; N, 6.79.

4-Chlorobenzaldehyde trisylhydrazone (1t): ^{1}H-NMR (DMSO-d_6) δ 11.83 (s, 1H), 7.91 (s, 1H), 7.54 (d, 2H, J = 8.6 Hz), 7.43 (d, 2H, J = 8.6 Hz), 7.23 (s, 2H), 4.22 (sept, 2H, J = 6.7 Hz), 2.89 (sept, 1H, J = 6.9 Hz), 1.89 (overlapping doublets, J = 7.0, 7.1 Hz); ^{13}C-NMR (DMSO-d_6) δ 152.70, 150.37, 143.48, 134.23, 132.77, 132.44, 128.79, 128.08, 123.58, 33.29, 29.16, 24.65, 23.32. Anal. Calcd for $C_{22}H_{29}N_2SO_2Cl$: C, 62.77; H, 6.94; N, 6.65. Found: C, 62.92; H, 6.93; N, 6.73.

4-Bromobenzaldehyde trisylhydrazone (1u): ^{1}H-NMR (DMSO-d_6) δ 11.80 (s, 1H), 7.92 (s, 1H), 7.52 (m, 4H), 7.22 (s, 2H), 4.25 (sept, 2H, J = 6.6 Hz), 2.90 (sept, 1H, J = 6.7 Hz), 1.23 (d, 12H, J = 6.6 Hz), 1.20 (d, 6H, J = 6.7 Hz); ^{13}C-NMR (DMSO-d_6) δ 152.52, 150.30, 143.40, 133.07, 132.40, 131.53, 128.20, 123.40, 122.87, 33.29, 29.09, 24.60, 23.26. Anal. Calcd for $C_{22}H_{29}N_2O_2SBr$: C, 56.77; H, 6.28; N, 6.02. Found: C, 56.58; H, 6.19; N, 6.11.

3-Bromobenzaldehyde trisylhydrazone (1v): ^{1}H-NMR (DMSO-d_6) δ 11.93 (s, 1H), 7.89 (s, 1H), 7.74 (s, 1H), 7.52 (t, 2H, J = 8.3 Hz), 7.32 (t, 1H, J = 7.9 Hz), 7.24 (s, 2H), 4.22 (sept, 2H, J = 6.7 Hz), 2.89 (sept, 1H, J = 6.9 Hz), 1.21 (d, 12H, J = 6.7 Hz), 1.18 (d, 6H, J = 6.8 Hz); ^{13}C-NMR (DMSO-d_6) δ 152.79, 150.40, 142.88, 136.24, 132.26, 130.88, 128.14, 126.05, 123.59, 122.07, 33.29, 29.19, 24.65, 23.31. Anal. Calcd for $C_{22}H_{29}N_2O_2SBr$: C, 56.77; H, 6.28; N, 6.02. Found: C, 56.84; H, 6.23; N, 6.06.

2-Bromobenzaldehyde trisylhydrazone (1w): ^{1}H-NMR (acetone-d_6) δ 10.71 (s, 1H), 8.41 (s, 1H), 7.86−7.82 (m, 1H), 7.60−7.56 (m, 1H), 7.39−7.24 (m overlapping s, 4H), 4.36 (sept, 2H, J = 6.8 Hz), 2.93 (sept, 1H, J = 6.9 Hz), 1.27 (d, 12H, J = 6.8 Hz), 1.21 (d, 6H, J = 6.9 Hz); ^{13}C-NMR (acetone-d_6) δ 154.01, 151.88, 144.50, 133.90, 133.83, 133.46, 132.16, 128.53, 127.86, 124.58, 124.10, 34.70, 30.51, 25.09, 23.70. Anal. Calcd for $C_{22}H_{29}N_2O_2SBr$: C, 56.77; H, 6.28; N, 6.02. Found: C, 56.88; H, 6.33; N, 6.10.

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4-Nitrobenzaldehyde trisylhydrazone (1x): ^{1}H-NMR (acetone-d_6) δ 11.19 (s, 1H), 8.24 (d, 2H, J = 8.8 Hz), 7.86 (d, 2H, J = 8.8 Hz), 7.32 (s, 2H), 4.36 (sept, 2H, J = 6.7 Hz), 2.94 (sept, 1H, J = 6.8 Hz), 1.28 (overlapping doublets, 18 H, J = 6.6, 6.7 Hz); ^{13}C-NMR (acetone-d_6) δ 154.25, 152.02, 149.21, 143.58, 143.49, 141.27, 133.51, 128.43, 124.73, 34.81, 30.63, 25.16, 23.77. Anal. Calcd for $C_{22}H_{29}N_3O_4S$; C, 61.23; H, 6.78; N, 9.74. Found: C, 61.13; H, 6.83; N, 9.82.

3-Nitrobenzaldehyde trisylhydrazone (1y): ^{1}H-NMR (DMSO-d_6) δ 12.10 (s, 1H), 8.37 (s, 1H), 8.17 (d, 1H, J = 7.9 Hz), 8.05 (s, 1H), 7.94 (d, 1H, J = 7.7 Hz), 7.66 (t, 1H, J = 7.9 Hz), 7.24 (s, 2H), 4.24 (sept, 2H, J = 6.7 Hz), 2.89 (sept, 1H, J = 6.9 Hz), 1.23 (d, 12H, J = 6.7 Hz), 1.17 (d, 6H, J = 6.8 Hz); ^{13}C-NMR (DMSO-d_6) δ 152.83, 150.43, 148.12, 142.33, 135.64, 133.09, 132.29, 130.35, 123.92, 123.62, 120.04, 33.29, 29.19, 24.64, 23.31. Anal. Calcd for $C_{22}H_{29}N_3SO_4$: C, 61.23; H, 6.77; N, 9.74. Found: C, 61.24; H, 6.72; N, 10.00.

2,4,6-Trimethylbenzaldehyde trisylhydrazone (1z): ^{1}H-NMR (DMSO-d_6) δ 11.53 (s, 1H), 8.17 (s, 1H), 7.21 (s, 2H), 6.79 (s, 2H), 4.18 (sept, 2H, J = 6.6 Hz), 2.88 (sept, 1H, J = 6.8 Hz), 2.15 (s, 3H), 2.09 (s, 6H), 1.17 (overlapping doublets, 18H, J = 6.75 Hz); ^{13}C-NMR (DMSO-d_6) δ 152.77, 150.31, 144.70, 138.09, 136.71, 129.24, 128.08, 123.50, 33.44, 30.73, 29.03, 24.67, 23.43, 20.64, 20.30. Anal. Calcd for $C_{25}H_{36}N_2O_2S$: C, 70.05; H, 8.46; N, 6.54. Found: C, 70.15; H, 8.50; N, 6.49.

General Procedure for Synthesis of Arylalkanes 3. The aldehyde tosylhydrazone (3.00 mmol) was dissolved in 17 mL of THF contained in an argon-flushed, 50 mL round-bottomed flask equipped with a side arm, reflux condenser, and stirring bar. Tributylborane (3.0 mmol, 3.0 mL of a 1.0 M solution in THF) was added via syringe, followed by NaOH (3.0 mmol, 1.0 mL of a 3.0 M solution in H_2O) or Bu_4NOH (3.0 mmol, 1.0 mL of a 3.0 M solution in MeOH). The reaction was heated to gentle reflux under argon and monitored by TLC for the disappearance of starting material. At the end of the reaction, as indicated by TLC, water (10 mL) was added to the reaction, and the mixture was allowed to cool to room temperature. The product **3** was extracted into ether. The combined organic layer were dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography.

The yields of **3** are presented in Tables 1 and 2. The physical and spectral properties of all products that had been previously reported were in accord with literature values and are summarized in the Supporting Information.

General Procedure for Synthesis of Aryl Alcohols 4. The aldehyde tosylhydrazone (3.00 mmol) was dissolved in 17 mL of THF contained in an argon-flushed, 50 mL, round-bottomed flask equipped with a side arm, reflux condenser, and stirring bar. Tributylborane (3.0 mmol, 3.0 mL of a 1.0 M solution in THF) was added via syringe, followed by DBU (0.45 mL, 3.0 mmol). The reaction was heated to a gentle reflux until the tosylhydrazone disappeared as evidenced by TLC. The reaction mixture was then oxidized by one of the following methods.

The yields of **4** are presented in Tables 3−7. The spectral properties of all products that had been previously reported were in accord with literature values and are summarized in the Supporting Information. The physical data for new compounds are presented below.

Oxidation with Sodium Perborate. The reaction vessel was placed in a room-temperature water bath. Distilled water (10 mL) and sodium perborate (1.38 g, 8.97 mmol) were then added. The reaction was stirred vigorously for 2 h. The reaction mixture was transferred to a separatory funnel and the product extracted into ether. The extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified via flash chromatography as described previously.

Oxidation with Peracetic Acid. The reaction vessel was placed in an ice−water bath. Peracetic acid (10 mmol, 2.2 mL of a 32 wt % solution in acetic acid) was added slowly over the course of 8 min. After the addition was complete, the ice bath was removed and the reaction mixture allowed to stir at room temperature for 1 h. A small amount of sodium thiosulfate solution was then added to destroy any excess peracid. The reaction mixture was transferred to a separatory funnel, extracted with ether (3 × 10 mL), washed with saturated sodium bicarbonate solution and then with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purifed via flash chromatography as described previously.

Oxidation with TMANO. The reaction vessel was cooled to room temperature, and TMANO (10 mmol, 5.0 mL of a 2.0 M solution in $CHCl_3$) was added. The mixture was then heated to reflux and allowed to remain at that temperature for 23 h. The mixture was then cooled and transferred to a separatory funnel, extracted with ether, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed, and the crude product was purified via flash chromatography as described previously.

1-(3-Nitrophenyl)pentan-1-ol (4k): ^{1}H-NMR ($CDCl_3$/TMS) δ 8.23−7.47 (m, 4H), 4.80 (t, 1H, J = 6.5 Hz), 2.16 (br s, 1H), 1.86−1.71 (m, 2H), 1.44−1.28 (m, 4H), 0.90 (t, 3H, J = 6.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.38, 147.08, 131.98, 129.31, 122.34, 120.86, 73.57, 39.02, 27.66, 22.49, 13.92. Anal. Calcd for $C_{11}H_{15}O_3N$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.98; H, 7.38; N, 6.42. The alkane product, 1-nitro-3-pentylbenzene (**3j**), was also isolated to give 0.13 g (23% yield).

6-Chloro-1-*p*-tolylhexan-1-ol (5aa): ^{1}H-NMR ($CDCl_3$/TMS) δ 7.22 (d, 2H, J = 8.1 Hz), 7.15 (d, 2H, J = 7.9 Hz), 4.62 (t, 1H, J = 6.6 Hz), 3.50 (t, 2H, J = 6.7 Hz), 2.34 (s, 3H), 1.89 (br s, 1H), 1.84−1.65 (m, 4H), 1.50−1.21 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 141.77, 137.22, 129.13, 125.79, 74.30, 44.95, 38.73, 32.49, 26.75, 25.10, 21.06. Anal. Calcd for $C_{13}H_{19}OCl$: C, 68.86; H, 8.45. Found: C, 68.77; H, 8.57.

7-Hydroxy-7-*p*-tolylheptanenitrile (5bb): ^{1}H-NMR ($CDCl_3$/TMS) δ 7.22 (d, 2H, J = 8.1 Hz), 7.16 (d, 2H, J = 8.1 Hz), 4.67−4.59 (dd, 1H, J = 6.1, 6.9 Hz), 2.38−2.27 (singlet and d, 5H, J = 7.0 Hz), 1.87−1.57 (m, 5H), 1.55−1.24 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 141.64, 137.32, 129.16, 125.76, 119.67, 74.21, 38.51, 28.49, 25.26, 24.96, 21.06, 17.02; IR (cm^{-1}, neat) 3450, 2950, 2855, 2250, 1518, 1460, 1425; GCMS m/z 199 (M − H_2O).

12-Hydroxy-12-*p*-tolyldodecanoic acid methyl ester (5cc): ^{1}H-NMR ($CDCl_3$/TMS) δ 7.22 (d, 2H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 4.61 (t, 1H, J = 6.7 Hz), 3.65 (s, 3H), 2.34 (s, 3H), 2.29 (t, 2H, J = 7.6 Hz), 1.91 (br s, 1H), 1.86−1.17 (m, 18H); ^{13}C-NMR ($CDCl_3$) δ 174.29, 141.99, 137.04, 129.04, 125.82, 74.48, 51.37, 39.00, 34.07, 29.45, 29.34, 29.17, 29.09, 25.81, 24.90, 21.05. Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 75.05; H, 10.14.

1-Chloro-6-*p*-tolylhexane (6aa): ^{1}H-NMR ($CDCl_3$/TMS) δ 7.07 (s, 4H), 3.51 (t, 2H, J = 6.7 Hz), 2.56 (t, 2H, J = 7.6 Hz), 2.31 (s, 3H), 1.76 (qt, 2H, J = 7.0 Hz), 1.61 (qt, 2H, J = 7.5 Hz), 1.56−1.30 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 139.47, 135.04, 128.94, 128.24, 45.07, 35.33, 32.55, 31.36, 28.48, 26.73, 20.96. Anal. Calcd for $C_{13}H_{19}Cl$: C, 74.09; H, 9.09. Found: C, 74.26; H, 9.24.

7-*p*-Tolylheptanenitrile (6bb): ^{1}H-NMR ($CDCl_3$/TMS) δ 7.13−7.01 (m, 4H), 2.57 (t, 2H, J = 7.6 Hz), 2.31 (singlet and t, 5H, J = 7.0 Hz), 1.68−1.30 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 139.24, 135.13, 128.97, 128.22, 35.25, 31.14, 28.51, 28.30, 25.29, 20.96, 17.07. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.41; H, 9.55; N, 6.82.

12-*p*-Tolyldodecanoic acid methyl ester (6cc): ^{1}H-NMR ($CDCl_3$/TMS) δ 7.07 (s, 4H), 3.66 (s, 3H), 2.55 (t, 2H, J = 7.7 Hz), 2.31 (s overlapping t, 3H and 2H, J = 7.5 Hz), 1.70−1.50 (m, 4H), 1.26 (br s, 14 H); 174.28, 139.83, 134.88, 128.86, 128.23, 51.37, 35.49, 34.09, 31.60, 29.52, 29.40, 29.36, 29.21, 29.12, 24.93, 20.94; ^{13}C-NMR ($CDCl_3$) δ. Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.67; H, 10.68.

***p*-Benzyltoluene (6ff):** ^{1}H-NMR ($CDCl_3$/TMS) δ 7.29−7.00 (m, 9H), 3.90 (s, 2H), 2.28 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 141.38, 141.23, 135.45, 129.10, 128.83, 128.39, 127.12, 125.93, 41.50, 20.94. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.68.

***trans*-5-*p*-Tolyl-4,5-dihydro-1*H*-pyrazole-3,4-dicarboxylic Acid Dimethyl Ester (10b).**[27] Dimethyl maleate **9** (0.435 g, 3.02 mmol) and **1b** (0.866 g, 3.00 mmol) were added to a flame-dried, argon-flushed, 50 mL, round-bottom flask equipped with a side arm, reflux condenser, stir bar, argon inlet, and mercury bubbler. Dry THF (20 mL) was then added followed by DBU (0.45 mL, 3.0 mmol) and the reaction heated to reflux for 1.5 h. The reaction was then cooled to room temperature and distilled water (10 mL) added. The reaction mixture was transferred to a separatory funnel, extracted with ether, washed with brine, and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure, and the crude product was flash chromatographed using 7 in. of silica gel in a 40 mm column with 25% EtOAc/hexanes to give 0.63 g (76% yield) of **10b**: ^{1}H-NMR ($CDCl_3$/TMS) δ 7.17 (s, 4H), 5.22 (d, 1H, J = 9.3 Hz), 4.02 (d, 1H, J = 9.3 Hz), 3.85 (s, 3H), 3.78 (s, 3H), 2.35 (s, 3H), 1.29−1.21 (br s, 1H); ^{13}C-NMR ($CDCl_3$) δ 170.86, 162.24, 138.63, 137.85, 136.24, 129.79, 126.10, 70.43, 57.93, 52.80, 52.25, 21.08.

Competition Experiment. The competition experiment was performed in the same manner as the synthesis of 1-*p*-tolylpentan-1-ol, **4b**, reported previously with the only difference being the addition of dimethyl maleate (0.433 g, 3.00 mmol) at the beginning of the reaction.

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Supporting Information Available: Melting points (Table 8) of all the (arenesulfonyl)hydrazones and ^{1}H NMR and ^{13}C NMR data (Table 9) for all alkane and alcohol products not described in the Experimental Section (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(27) For the preparation and spectra of compounds similar to **10b** see: (a) Hassner, A.; Michelson, M. J. *J. Org. Chem.* **1962**, *27*, 3974. (b) Jones, W. M. *J. Am. Chem. Soc.* **1959**, *81*, 3776, 5153. (c) Jones, W. M.; Sanderfer, P. O.; Baarda, D. G. *J. Org. Chem.* **1967**, *32*, 1367.