Detailed Characterization of *p*-Toluenesulfonic Acid Monohydrate as a Convenient, Recoverable, Safe, and Selective Catalyst for Alkylation of the Aromatic Nucleus

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Alkylation of the aromatic nucleus, an important reaction in industry and synthetic organic chemistry, has traditionally been carried out by the well-known Friedel−Crafts reaction employing Lewis acid catalysts such as $AlCl_3$ and BF_3 or by using highly reactive organometallic reagents. Although protic acids such as anhydrous HF and concentrated H_2SO_4 have also been used in the alkylation of the aromatic nucleus, the notoriously corrosive, highly toxic, and hazardous nature of these agents has precluded their common use under ordinary laboratory conditions. Various organic sulfonic acids have, on occasion, been used as catalysts in Friedel−Crafts alkylations, but to our knowledge the chemistry and the scope of these reactions for common laboratory use have never been exploited in detail. In the present study we have characterized commercially available *p*-toluenesulfonic acid monohydrate (TsOH) as an efficient catalyst for the intermolecular coupling of the aromatic nucleus with activated alkyl halides, alkenes, or tosylates under mild conditions in an open atmosphere. In comparison to conventional Friedel−Crafts catalysts such as $AlCl_3$, BF_3, HF, and concentrated H_2SO_4, the extent of the formation of undesired products from side reactions such as transalkylation, polymerization, etc. was minimal with the TsOH-catalyzed reaction. The ability to recover and reuse the catalyst from the reaction mixtures, minimal generation of environmentally unfriendly waste, high specificity of the reaction, and the low cost of the catalyst are important advantages of the TsOH catalyst over the other conventional Friedel−Crafts catalysts.

Introduction

Alkylbenzenes and alkylphenols are important raw materials in industry and in scientific research. For example, alkylbenzenes with 10−14 side chain carbon atoms are starting materials for the manufacture of sulfonates which are important raw materials for the industrial production of anion-active detergents and polymers.[1] Annual production of alkylbenzenes for this purpose is estimated to be over one million tons in Western Europe, USA, and Japan. On the other hand, alkylphenols are widely employed as antioxidant and antibacterial agents.[2]

Alkylation of the aromatic nucleus has been traditionally carried out with the well-known Friedel−Crafts reaction using Lewis acids or organometallic reagents using the corresponding alkyl halides.[3] In the course of more than 100 years of Friedel−Crafts chemistry, only two catalysts, $AlCl_3$ and BF_3, have gained wide recognition.[4] Especially, anhydrous $AlCl_3$ maintained its wide use ever since it was introduced by Friedel and Crafts,[3] despite some unfavorable properties such as limited solubility in organic solvents and sublimation at higher temperatures, in solution chemistry. In addition, in some cases $AlCl_3$ is known to result in extensive undesirable side reactions such as degradation, polymerization, and isomerization, causing the reduction of expected product yields significantly. Boron trifluoride has also become a widely used catalyst since the 1920s following initial studies by Meerwein, Nieuwland, and others.[4,5] Since BF_3 is a low-boiling gas (bp −101 °C), some of its more convenient complexes such as ether complexes are frequently used despite their low reactivity. Although a significant number of other Lewis acid halides and pseudohalides are also used in Friedel−Crafts reactions, none of them have achieved the wide applicability in solution chemistry that $AlCl_3$ and BF_3 have.[4]

Although various other methods for alkyl substitution in the aromatic nucleus have also been exploited, still no common convenient method which is suitable for a majority of alkyl substituents is available. For example, until recently, no simple and mild method has been described for the intermolecular arylation of cyclic and bicyclic substrates.[6] In recent years, a number of studies on aromatic substitution using olefins by the action of organometallic reagents, especially palladium and copper

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containing,[7] have been reported. However, the usefulness of these sensitive organometallic reagents under ordinary laboratory conditions is limited by the rigorous inert conditions required and the relatively high cost of the metal catalysts used in these reactions. On the other hand, although protic acids such as anhydrous HF and concentrated H_2SO_4 have also been successfully used in the alkylation of the aromatic nucleus using simple olefins,[8] the notoriously corrosive, highly toxic, and hazardous nature of these agents has precluded their common use under ordinary laboratory conditions.

Various organic sulfonic acids[4,9] including perfluorosulfonic acids[9a,b] (superacids), methanesulfonic acid,[9c] and benzenesulfonic acid[9d] have, on occasion, been used as catalysts in Friedel−Crafts alkylations. In addition, *p*-toluenesulfonic acid (TsOH) has also been occasionally used as a Friedel−Crafts alkylation catalyst[9f−n] (mainly for the alkylation of phenols[9i−l] and other highly activated aromatic nuclei[9g,h]). However, to our knowledge the chemistry and the scope of these reactions for common use have never been exploited in detail. For example, TsOH has not been described as a useful catalyst for the alkylation of the aromatic nucleus with haloalkanes, haloalkenes, alkyl sulfonates, or cycloalkenes. The lack of the popularity of TsOH as a Friedel−Crafts alkylation catalyst is also quite apparent from the fact that the most recent review by Olah et al.[4c] on the subject has not even cited TsOH as a catalyst for the reaction.

In the present study we have carried out a systematic characterization of the alkyl substitution of the aromatic nucleus using commercially available *p*-toluenesulfonic acid monohydrate (TsOH) as a catalyst. Our results demonstrate that TsOH is a very effective environmentally friendly catalyst for the alkylation of the aromatic ring with activated aliphatic halides, alkenes, and sulfonic esters. While this reaction could be carried out in an open atmosphere to produce high yields of the desired products, most of the catalyst could be recovered by simple filtration and reused. The scope and mechanism of the reaction is discussed in detail.

Results and Discussion

Alkylation of the toluene nucleus by various alkylating agents was chosen as a model reaction for our study. The standard reactions were carried out in an open pot under refluxing conditions using the desired alkyl substrate, toluene (also the solvent), and the catalyst, TsOH. To explore the scope and the selectivity of the reaction, three different types of alkylating reagents (Scheme 1), allylic and activated halides (type A), tosylates (types B, E, and F), and cyclic (type C) and acyclic (types D and G) alkenes, have been used as substrates. In addition to these, we have also used secondary, tertiary, and benzyl halides as alkyl substrates to further examine the selectivity and the scope of the reaction and to compare and contrast with the corresponding conventional Friedel−Crafts alkylations (Scheme 1 and Table 1).

Initial experiments indicated that TsOH is an effective recoverable catalyst for the alkylation of toluene with the above listed alkyl substrates. Studies of the effects of catalyst concentration (0.3−2.2 equiv) on the distribution and yield of the products showed that, while substoichiometric amounts of the catalyst are effective in promoting the reaction, the use of higher concentrations reduced the reaction time considerably. An optimum ratio of catalyst to alkyl substrate was estimated to be about 1:1.2. However, the use of increased amounts of the catalyst neither decreased the yield nor promoted the side reactions such as polymerization, which is a common problem with most other conventional Friedel−Crafts catalysts. For example, in the case of alkene arylation, most protic acid catalysts form byproducts, believed to be the alkyl esters of the catalyst, which promote polymerization upon heating and lead to a significant reduction in the yield of the reaction.[10] Although TsOH also produces tosylate byproducts[11] from alkenes under the reaction conditions used, these tosylates were also found to be excellent substrates for the alkylation reaction, giving the same products as the original olefin (see below) rather than the polymerized products.

Most conventional Friedel−Crafts catalysts generally give complex reaction mixtures which could be worked up and separated with difficulty[12] and with the loss of generally expensive catalysts, producing environmentally unfriendly, toxic waste. In contrast, TsOH is completely soluble in most aromatic solvents such as toluene under refluxing conditions to give homogeneous solutions, and when the reaction mixture is cooled to room temperature, most of the TsOH separates as a crystalline solid. More than 75% of the solid catalyst could be conveniently recovered at the end of the reaction by simple filtration, and the catalyst could be reused without any loss of catalytic activity. Simple solvent extraction of the reaction mixture with hexane and a solution of 0.1 M sodium bicarbonate removes the small contamination of the catalyst, and evaporation of the hexane extract yields a relatively clean crude mixture of products.

Alkylation of Toluene by Haloalkenes. Unsaturated alkyl halides such as allylic halides possess two reactive centers susceptible to Friedel−Crafts alkylation. It is known that these haloalkenes react either at the double bond or at the allylic center depending on the type of catalyst and the reaction conditions used.[13] While

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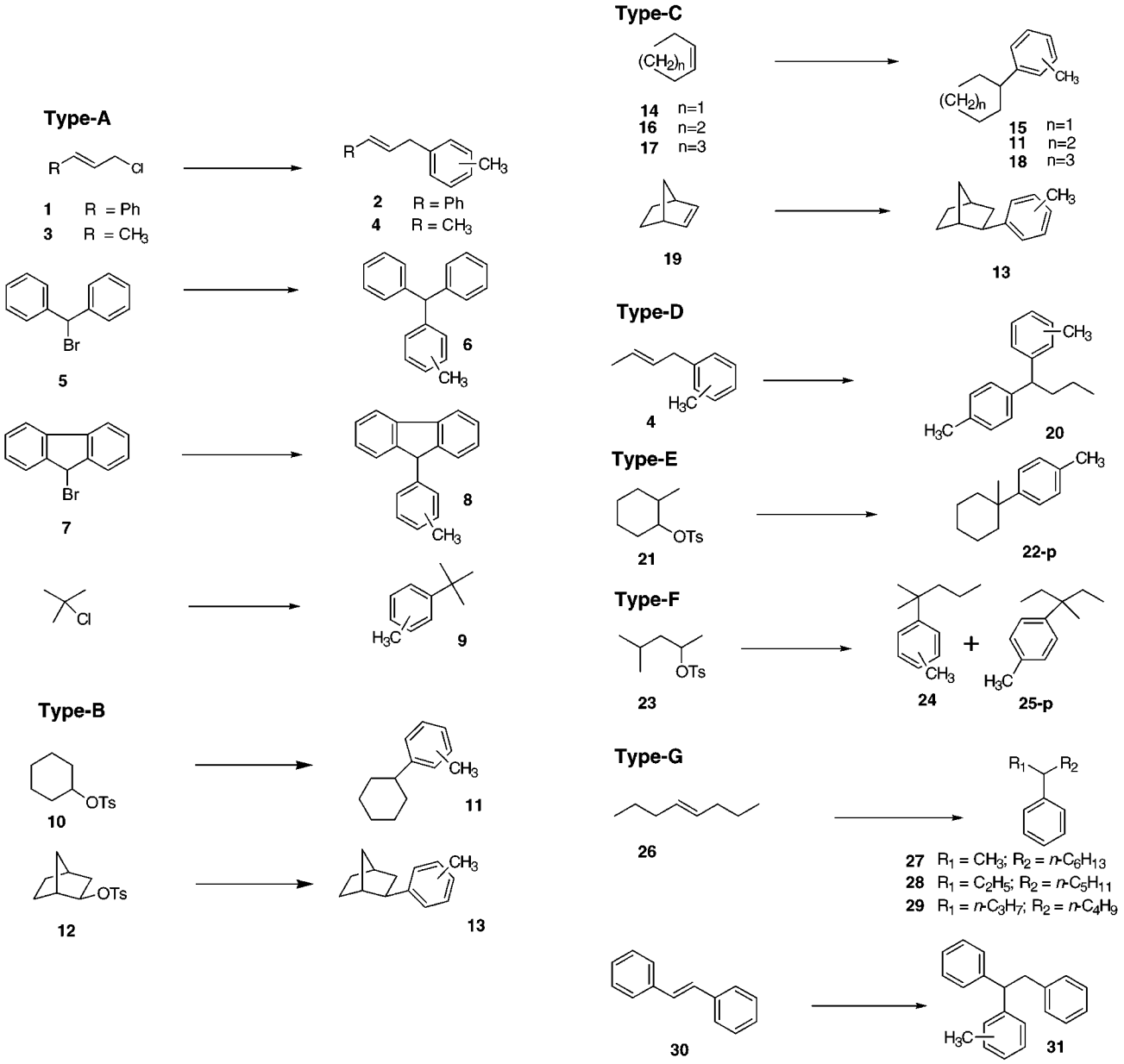
Scheme 1



protic catalysts such as H_2SO_4 generally favor the reaction at the double bond, less reactive metal halide catalysts such as $ZnCl_2$ and $FeCl_3$ favor the reaction at the allylic position initially and then the electrophilic addition of the aromatic nucleus to the double bond. To examine the selectivity of the TsOH-catalyzed alkylation reaction, we have initially examined *trans*-cinnamyl chloride (**1**) as an alkyl substrate under the standard reaction conditions (type A, Scheme 1). These studies revealed that **1** is an excellent substrate for the reaction and produces *trans*-1-phenyl-3-tolyl-1-propenes (**2**; entry 1, Table 1) as the exclusive product, in excellent yield (98%) under the conditions used. We believe the high selectivity of the reaction toward the allylic position must be a consequence of the extra stability of the double bond of **1** due to the direct conjugation with the phenyl ring and the mild nature of the reaction conditions used. In addition, we note that, to our knowledge, this is the first example of the direct arylation of any cinnamyl halide and the first one-step preparation of unsymmetrical 1,3-diarylpropenes from commercially available starting materials. The simplicity of the procedure makes this method even more attractive over the other methods reported in the literature.[14]

As expected, *trans*-crotyl chloride (**3**) also behaves in a similar manner to that of **1**, but with less reactivity and selectivity (entries 2−5, Table 1), giving relatively low yields of *trans*-1-tolyl-2-butenes (**4**) as the initial products (entries 2 and 3, Table 1) at shorter reaction times. Prolongation of the reaction time (entries 4 and 5, Table 1) results in the formation of 1,1-ditolylbutane (**20**; type D, Scheme 1) which was rather unexpected since most reported disubstituted products from allylic halides are 1,2-diarylalkanes.[13] However, under mild reaction conditions formation of the 1,1-aryl product is expected since the benzylic carbenium ion **4c** from the initial product (**4**) is more stable than the other possible

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Table 1. Alkylation of Toluene in the Presence of *p*-Toluenesulfonic Acid[a]

entry	substrate	time (h)	products	% convn[b]	% total yield[c]	% isomer ratio (o, m, p)[d]
1	**1**	3	**2**	100	>98	35, -, 65
2	**3**	1	**4**	33	~90	-
3	**3**	3	**4**	67	~91	37, 4, 59
4	**3**	9	**4**, **20** (66%)	85	~95	-
5	**3**	18	**20**	100	100	46(op), -, 54(pp)
6	**5**	6	**6**	100	100	19, 3, 78
7	**7**	12	**8**	100	~99	16, 0, 84
8	**10**	3	**11**	42	100	27, 17, 56
9	**10**	18	**11**	100	100	28, 18, 54
10	**12**	18	**13**	100	100	34, 18, 48
11	**21**	1.5	**22**	54	100	-
12	**21**	3	**22**	100	100	-, tr, >99
13	**23**	18	**24** (86%),[e] **25**	100	100	-, 4, 96
14	**14**	4	**15**	100	85	33, 23, 44
15	**16**	6	**11**	100	98	29, 18, 53
16	**17**	6	**18** (65%),[e] **22**	100	87	30, 21, 49
17	**19**	5	**13**	100	100	34, 18, 48
18	**30**	48	**31**	100	97	~16, tr, 84
19	**33**	3	**11**	tr	-	-
20	**33**	84	**11**	50	80	-
21	*t*-BuCl	30	**9**	-	40[f]	0, 5, 95
22	**34**	60	**35**	32	100	35, 25, 40

[a] Reactions were carried out with ~1 M solutions of the substrate and 1.2 molar equiv of *p*-toluenesulfonic acid in toluene. [b] Calculated from the ^{1}H NMR of the crude products. [c] Isolated yield with respect to the % conversion. [d] Calculated from the intensity of the corresponding ^{1}H NMR signals of un-isoltated product mixtures. [e] o, m, p isomer ratios indicated are for these major products. [f] Significant amount of the substrate may have been lost during the reaction due to the low boiling point.

isomeric carbenium ions[15] (Scheme 2). Isolation of trace amounts of *trans*-1-(2-methylphenyl)-1-butene (**32-o**) from the reaction mixture confirms that **20** must be arising from the acid-assisted double bond migration[13,15] of the initially generated carbenium ion **4a** to produce **4c** followed by a simple acid-assisted second arylation (Scheme 2; also see alkene arylation; entries 14−18, Table 1). In addition, the absence of diortho product of **20**, 1,1-bis(2-methylphenyl)butane, suggests that the arylation of **4** is strongly dependent on steric factors. To our knowledge, 1,1-diarylalkanes, except 1,1-diarylethane from vinyl chloride[16] and styrene,[17] are not commonly obtained from a one-step reaction of conventional Friedel−Crafts alkylation conditions using allylic halides or any other common substrates in good yield.

Alkylation of Toluene by Alkenes. Since cyclic olefins usually behave in a manner similar to that of their acyclic counterparts as alkyl substrates in Friedel−Crafts reactions (except the possible ring contraction or expansion side reactions), and since cyclic alkenes could be more reactive toward electrophiles due to the extra torsional energy of the ring double bond, we predicted that cyclic alkenes could also be good alkyl substrates for TsOH-catalyzed alkylation of the aromatic nucleus. As expected, TsOH-catalyzed catalyzed alkylation of toluene by monocyclic and bicyclic alkenes (type C, Scheme 1) proceeds remarkably well, giving high yields of the desired products (entries 14−18, Table 1). In addition, cycloheptene (**17**) undergoes alkylation quite readily (entry 16, Table 1) to give a mixture of products, tolylcycloheptane (**18**; 65%) and the ring-contracted product 1-methyl-1-*p*-tolylcyclohexane (**22-p**; 35%), with an 87% total yield.[18] The ratio of the two products, **18** to **22-p,** is not significantly dependent on the reaction time (18 h). In addition, prolonged refluxing of **22-p** in the presence of TsOH in either toluene or xylenes did not cause further ring contraction or expansion of the compound and the starting material, **22-p,** was isolated almost quantitatively. In contrast to the behavior of **17**, cyclohexene (**16**) exclusively gave tolylcyclohexane (**11**; entry 15, Table 1), with no evidence of the ring-contracted products.[19] These results further confirm the early observation that while $AlCl_3$-catalyzed alkylation of cycloheptene predominantly produces 1,3- and 1,4-substituted cyclohexanes[20] as ring-contracted products, protic acids such as H_2SO_4[21] and TsOH give 1,1-substituted cyclohexanes and/or cyclopentanes.

Alkylation of Toluene by Alkyl Tosylates. Although alkyl arenesulfonates, particularly alkyl tosylates, are very active alkylating agents compared to the corresponding alkyl halides, their use in conventional Friedel−Crafts alkylation is not widespread. Since TsOH-mediated alkylation appears to proceed through a carbenium ion intermediate, we have examined several secondary tosylates (types B, E, and F, Scheme 1) as possible alkyl substrates, since these may also easily produce the corresponding carbenium ions under these reaction conditions. As expected, both cyclohexyl (**10**; entry 9, Table 1) and *exo*-2-norbornyl (**12**; entry 10, Table 1) tosylates gave the expected products (**11** and **13**, respectively) in quantitative yields. However, when *trans*-2-methyl-1-(tosyloxy)cyclohexane (**21**; entry 12, Table 1) or *trans*-1-(benzenesulfonyloxy)-2-methylcyclohexane was used as the alkyl substrate (type E, Scheme 1), the coupling took place smoothly within a short period of time to give the unexpected 1,1 isomer **22-p** as the sole product in 100% yield rather than the 1,2 isomer. The acyclic counterpart, 4-methyl-2-(tosyloxy)pentane (**23**; entry 13, Table 1) or 2-(benzenesulfonyloxy)-4-methylpentane, while requiring a longer reaction time (18 h) for the quantitative conversion, yielded two structural isomers (type F, Scheme 1), 2-methyl-2-tolylpentane (**24**; 86%) and 3-methyl-3-*p*-tolylpentane (**25-p**; 14%). The notable feature of the latter reaction is the very high proportion of **24** over **25** despite the fact that both must have been derived from the electrophilic arylation of tertiary alkyl carbenium ions.

Alkylation of Toluene by Active Alkyl Halides. Unactivated alkyl halides were found to be not as reactive as tosylates toward the TsOH-catalyzed arylation reaction (entries 19−22, Table 1). For example, bromocyclohexane (**33**; entry 20, Table 1) needed 84 h for 50% conversion to **11** with 80% yield, while only 32% of benzyl chloride (**34**; entry 22, Table 1) was converted to phenyltolylmethane (**35**) in 60 h. However, the activated halide bromodiphenylmethane (**5**; type A, Scheme 1) undergoes arylation much more efficiently and quantitatively to yield the corresponding diphenyltolylmethane (**6**; entry 6, Table 1) within 6 h. Similarly, 9-bromofluorene (**7**; type A, Scheme 1) is also converted to the corresponding

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(18) Careful ^{1}H and ^{13}C NMR analysis unequivocally confirmed the structure of **22-p** which is identical to the product obtained from the tosylate **21** (entry 12, Table 1).
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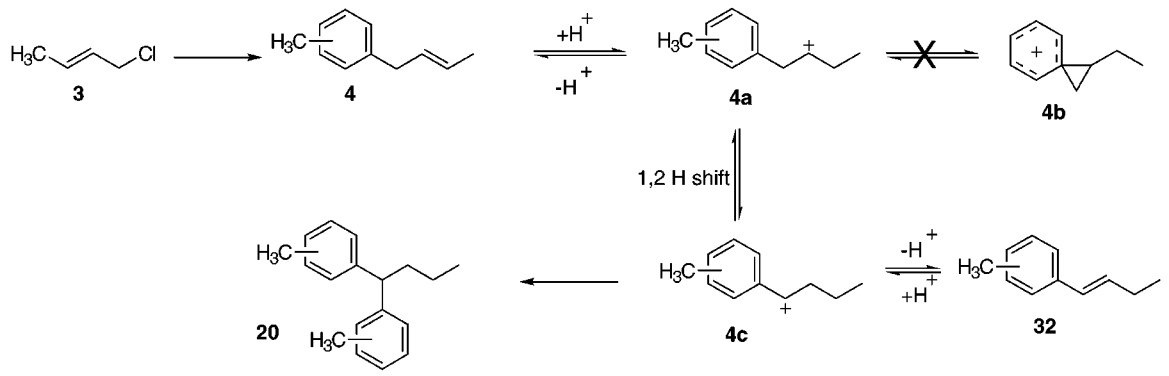
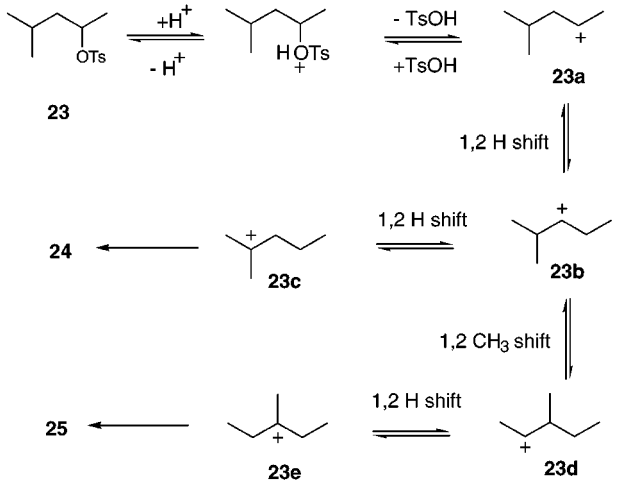
Scheme 2



9-tolylfluorene (**8**) under the standard reaction conditions in excellent yield (99%; entry 7, Table 1) after 12 h of refluxing. Although both **5** and **7** have very similar electronic and steric properties, the above results indicate that the arylation of **7** is somewhat slower than that of **5**. We believe this significant difference in reactivity may primarily be due to the steric effect. In addition, no meta isomer was detected in the reaction of **7** in contrast to the reaction of **5** where about 3% of the meta isomer was produced. These results, especially the difference in relative reactivities of **5** and **7**, may provide important information about the detailed mechanism of the TsOH-catalyzed aromatic alkylation reaction. In addition, we emphasize that 9-arylfluorene has not been previously obtained by the Friedel−Crafts alkylation reaction using conventional Lewis acid or protic acid catalysts. The major product from **7**, 9-(4-methylphenyl)fluorene (**8-p**; 84%), was easily purified by simple column chromatography. The other 16% of the product was exclusively the ortho isomer, **8-o**, which was identified by characteristic deshielding of 9-H (5.33 ppm of **8-o** vs 5.00 ppm of **8-p**) and benzylic-CH_3 (2.71 vs 2.30 ppm) proton signals in ^{1}H NMR and shielded 9-C (50.00 vs 54.09 ppm) and benzylic-CH_3 (20.41 vs 21.05 ppm) signals in ^{13}C NMR.[22]

Review of the Mechanism. Although stereochemical and mechanistic studies of the Friedel−Crafts reaction have been limited, the generation of a complex species with carbenium ion character from the alkyl substrate is commonly accepted.[23] The formation of most of the products from TsOH-catalyzed reactions (types B−G, Scheme 1) could also be best explained by assuming the formation of an initial carbenium ion intermediate,[24] even though a free radical mechanism could also be possible under the thermal and nonpolar reaction conditions used. We believe TsOH is capable of generating a carbenium ion intermediate from most of the alkyl substrates tested at higher temperatures which could readily undergo electrophilic substitution (before or after skeletal rearrangement) with the readily available aromatic solvent. The initial carbenium ion intermediate could possibly be generated by acid-catalyzed elimination of the tosyloxy group (types B, E, and F, Schemes 1 and 3) or electrophilic addition of a proton to the double bond (types C, D, and G, Schemes 1, 2, and 4) under appropriate

Scheme 3

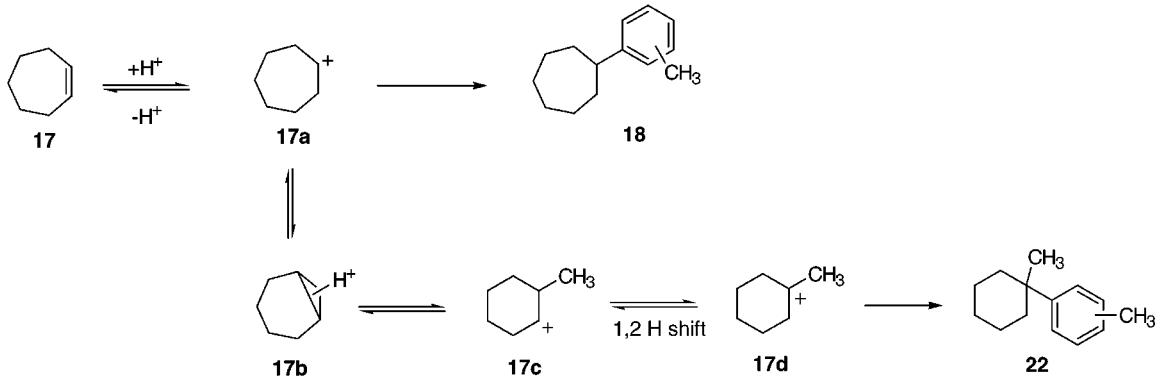


reaction conditions.[25] Furthermore, careful inspection of the reactivities of various substrates, especially the reactions which could generate identical (e.g., entries 9, 15, and 20 or 10 and 17, Table 1) or energetically similar (e.g., entries 6 and 7 or 9 and 12, Table 1) initial carbenium ion intermediates indicate that the relative reactivities of the carbenium ions do not correlate with the observed rates of the reactions, suggesting that the initial carbenium ion generation step may be the rate-determining step.[26a] Formation of carbon skeleton rearranged, thermodynamically more stable products also provides further support for a SN1[27] type two-step mechanism for the reaction.

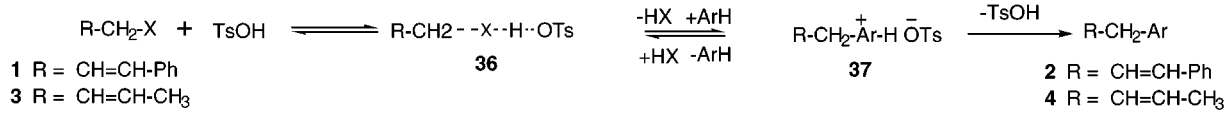
The carbon skeleton rearrangement in the Friedel−Crafts reaction is well-documented. The most important driving force for the formation of only two rearranged products, **24** and **25**, from alkyl substrate **23**, which would presumably generate carbenium ion **23a** initially (Scheme 3), must be the thermodynamic stability of the tertiary carbenium ions **23c** and **23e** over the secondary carbenium ions **23a**, **23b**, and **23d**.[27] The product, **24**, must arise from the tertiary carbenium ion **23c**, which could be generated from **23a** by two successive 1,2 hydride shifts (Scheme 3). On the other hand, **25** could

(22) Nakamura, M.; Nakamura, N.; Oki, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1097.
(23) Hart, H. In ref 4a, 1963; Vol. I, Chapter 13, pp 999−1015.
(24) Gates, B. C. *Catalytic Chemistry*; John Wiley & Sons: New York, 1992.
(25) However, generation of a carbenium ion intermediate from type A alkyl substrates could not be easily envisioned.
(26) (a) Brown, H. C.; Grayson, M. *J. Am. Chem. Soc.* **1953**, *75*, 6285. (b) Brown, H. C.; Jungk, H. *J. Am. Chem. Soc.* **1955**, *77*, 5584. (c) Brown, H. C.; Jungk, H. *J. Am. Chem. Soc.* **1956**, *78*, 2182. (d) Jungk, H.; Smoot, C. R.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 2185.
(27) Nenitzescu, C. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; John Wiley-Interscience: New York, 1968; Chapter 1, Vol. I, pp 1−75.

Scheme 4



Scheme 5



arise from the symmetrical tertiary carbenium ion **23e** presumably generated by successive 1,2 hydride and methide shifts followed by a second 1,2 hydride shift (Scheme 3). The predominant formation of **24** over **25** must be at least partly due to the relatively slow rate of formation of **23e** in comparison to **23c** as a consequence of a slow 1,2-methide shift relative to the competing 1,2-hydride shift. In addition, other steric and electronic factors such as hyperconjugation may also play an important role in the overall product distribution of the reaction. The high sensitivity of the reaction toward steric and electronic factors[27,28] is also clearly reflected in the observed product distribution of 4-octene[29] (**26**; type G, Scheme 1). The observed high percentage of 2-phenyloctane (**27**; 65%) in comparison to 3- and 4-phenyloctanes [**28** (21%) and **29** (15%), respectively] could be due to the steric preference of the arylation step. The absence of ortho products derived from the tertiary carbenium intermediates further suggests that the isomer ratio of the final product is mainly determined by the steric factors (entries 12−13 and and 21, Table 1).

Formation of **20** as the only product from the alkyl substrate **2** in high yield at longer reaction times (entry 5, Table 1) is intriguing and has not been observed with conventional Friedel−Crafts alkylation reactions.[13,15] Examination of the product distribution with time (entries 2−5, Table 1) further indicates that arylation initially occurs at the allylic position of the substrate, although initial alkylation of H_2SO_4-catalyzed reactions is known to predominantly occur at the double bond.[13] In addition, although the nonclassical bridged carbenium ion **4b** (Scheme 2) which is proposed to be characteristic under acid-catalyzed Friedel−Crafts reaction conditions[4c,27,30] should lead to the formation of only the 1,2-diaryl products, **3** gives 1,1-diarylbutane (**20**) as the sole product. These results appear to suggest that carbenium ion **4b** may not be present under our reaction conditions[30] (Scheme 2). As shown in Scheme 2, we believe that the observed 1,1-diarylated products could simply be generated from the resonance-stabilized benzylic carbenium ion **4c** which may be generated by a 1,2-hydride shift of the initially produced, relatively less stable carbenium ion **4a**.

In the literature there is no detailed discussion on the rearrangement of initially produced cycloheptylium ion (**17a**, Scheme 4) during the Friedel−Crafts alkylation from **17**. Reported rearranged products of **17** in the Friedel−Crafts reaction are, however, 1-aryl-3-methyl- and 1-aryl-4-methylcyclohexanes with $AlCl_3$ as the catalyst (none reported with protic acid catalysts such as H_2SO_4 and HF), and to our knowledge, there is no strong evidence for the formation of 1-aryl-1-methylcyclohexane.[15] The production of **22-p** in addition to **18** in the reaction of **17**, even under the relatively milder conditions used, is therefore highly intriguing. The formation of **22-p** as a rearranged product from **17** could be rationalized by proposing that the initially formed **17a** may be first isomerized to the carbenium ion **17c** by a Wagner−Meerwein type rearrangement through ring opening of the protonated cyclopropyl intermediate **17b** and then a 1,2-hydride shift[31,32] to produce the more stable tertiary carbenium ion **17d** followed by electrophilic attack on toluene (Scheme 4). Lack of further ring-contracted, cyclopentane products[32] suggests that both the 1,2-hydride shift and arylation steps must be faster than the possible further ring contraction reactions of **17c** and **17d**.[33] The ratio of products **18** to **22-p** (65% to 35%) may, therefore, indicate the relative thermodynamic stabilities and the reaction rates of ions **17a** and **17b**.

At present we do not have a reasonable mechanism for type A reactions, since acid-catalyzed formation of an isolated carbenium ion could not be easily justified for this type of reaction. The absence of free carbenium ion in these reactions is strongly supported by the observation that only **2** and **4** (Scheme 5) are formed from **1** and **3**, respectively, without other possible carbenium ion rearranged products such as 3-phenyl-3-tolyl-1-propene

(28) McCaulay, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 6437.
(29) In this reaction, benzene was used instead of toluene to avoid further complication of the product distribution due to the formation of ortho, meta, and para isomers of the products.
(30) Ransley, D. L. *J. Org. Chem.* **1966**, *31*, 3595.
(31) Weitkamp, J.; Ernst, S. In *Catalysis by Acids and Bases*; Imelik, B., Naccache, C., Coudurier, G., Taarit, Y. B., Vedrine, J. C., Eds.; Elsevier Science Publishers B.V.: Amsterdam, The Netherlands, 1985; pp 419−426.
(32) Guisnet, M. In ref 31, 1985, pp 283−297.
(33) This proposal is also consistent with the observation that **22-p** is the only product from **21**.

from **1** and 3-tolyl-1-butene from **3**[13] (Scheme 5). Therefore, the formation of only **2** from **1** and **4** from **3** could only be explained by considering the Friedel−Crafts reaction as a displacement type reaction as proposed by Brown and co-workers[26] (Scheme 5). For example, initially formed alkyl halide−TsOH adduct **36** does not ionize until nucleophilic attack of arene takes place to form the complex **37**, avoiding the possibility of a rearrangement of the carbon skeleton.[26a] Although this interpretation is reasonable and in good agreement with the product isolated, it is clear that further study is necessary to propose a detailed mechanism for these types of reactions. In addition, the formation of **2** and **4** from **1** and **3**, respectively, at shorter reaction times demonstrates that the allylic halide functionality is more reactive than the double bond under these reaction conditions.

Selectivity. The results presented in Table 1 clearly demonstrate that unactivated primary and secondary alkyl halides are much less reactive than the corresponding arenesulfonate esters under identical reaction conditions (see entries 8 and 19; Table 1). On the other hand, alkenes are generally much more reactive than either alkyl halides or arenesulfonate esters under similar experimental conditions (entries 9, 15, and 20; Table 1). In addition, alcohols were found to be completely inactive toward the TsOH-catalyzed alkylation under the above conditions, unexpectedly.[9m,n] Therefore, TsOH could be used to arylate either alkene- or arenesulfonates selectively, conveniently and efficiently, in the presence of unactivated primary and/or secondary halide and/or alcohol groups. Furthermore, entries 2−5 in Table 1 clearly show that further selectivity of the desired products can be obtained by carefully controlling the reaction conditions. We also note that although cyclohexenes are excellent substrates for the reaction, 2-cyclohexenone is completely inactive under the same reaction conditions, probably due to the slight deactivation of the double bond toward protonation. Similarly, both ethyl 2-(tosyloxy)propanoate and ethyl 2-bromopropanoate failed to alkylate toluene or xylene and instead both underwent de-esterification during extended reaction times (3 days), further suggesting that even slightly deactivated tosylates or halides are not good alkyl substrates for TsOH-catalyzed aromatic alkylation reactions. These observations strongly suggest that TsOH-catalyzed aromatic alkylation could also be carried out selectively in the presence of such slightly deactivated tosyl and halide groups.

Taken together, the present studies have clearly shown that TsOH could be used as an efficient catalyst in the intermolecular coupling of the aromatic nucleus with activated alkyl halides, alkenes, or tosylates under relatively mild conditions in an open atmosphere. All the model reactions which were carried out using toluene as the aryl substrate resulted in excellent yields of coupled products. In contrast to conventional catalysts such as $AlCl_3$, BF_3, HF, and concentrated H_2SO_4 catalyzed Friedel−Crafts reactions, the extent of the formation of undesired products from side reactions such as transalkylation, polymerization, etc. was minimal with the TsOH-catalyzed reaction. The ability to recover and reuse the catalyst from the reaction mixtures, minimal generation of environmentally unfriendly waste, high specificity of the reaction, and the low cost are important advantages of the TsOH catalyst over the other conventional Friedel−Crafts catalysts. Studies of the scope and the synthetic utility of this reaction with more functionalized analogues of aromatic substrates are in progress.

Experimental Section

General. All ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) were recorded in $CDCl_3$ with TMS as an internal standard. All chemical shifts were reported on the δ (ppm) scale relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.00 ppm) for ^{13}C NMR. All the coupling constants (J) were in hertz. Unless otherwise noted, commercially available chemicals with at least 98% purity were used throughout this study. All solvents were reagent grade and freshly distilled. The notations **-o**, **-p**, **-m** following the compound numbers indicate the ortho, para, and meta isomers of the products with respect to the methyl substituent in the aromatic ring.

General Procedures. Tosylation of Alkyl Alcohols. A mixture of alcohol (0.05 mol) and *p*-toluenesulfonyl chloride (11.4 g, 0.06 mol) in 25 mL of carbon tetrachloride was stirred for 15 min. Dried triethylamine (7.6 g, 0.075 mol) was then added dropwise, and the mixture was stirred for 4 h. The solid amine hydrochloride was separated by filtration, and the filtrate was washed several times with distilled water and dried over anhydrous Na_2SO_4. The evaporation of the solvent in vacuo yielded a crude solid which was purified by column chromatography.

Alkylation of Toluene. A mixture of the desired alkyl substrate (0.05 mol) and *p*-toluenesulfonic acid monohydrate (11.4 g, 0.06 mol) in 53 mL of toluene (0.5 mol) was refluxed for the appropriate times indicated in Table 1, with magnetic stirring. The reaction mixture was cooled to room temperature, allowing the crystalline catalyst to separate. The solid catalyst was then filtered and washed with hexane (2 × 25 mL). The resultant organic filtrate was washed first with 0.1 M $NaHCO_3$ solution and then with distilled water and dried over anhydrous Na_2SO_4. The evaporation of the organic solvent in vacuo yielded crude product mixtures which were subjected to further purification whenever it was appropriate.

Alkylation of Toluene with *trans*-Cinnamyl Chloride (1). 3-(4-Methylphenyl)-1-phenylpropene (2-p). ^{1}H NMR: δ 2.32 (3H, s), 3.50 (2H, d, J = 6.84), 6.34 (1H, dt, J = 15.74, 6.40), 6.42 (1H, d, J = 15.87), 7.03−7.21 (5H, m), 7.23−7.36 (4H, m). ^{13}C NMR: δ 21.00 (q), 38.92 (t), 126.11 (d), 127.02 (d), 128.46 (d), 128.54 (d), 129.18 (d), 129.53 (d), 130.87 (d), 135.65 (s), 137.07 (s), 137.58 (s).

3-(2-Methylphenyl)-1-phenylpropene (2-o). ^{1}H NMR: δ 2.32 (3H, s), 3.52 (2H, d, J = 5.32), 6.33 (1H, dt, J = 15.84, 5.26), 6.36 (1H, d, J = 15.87), 7.03−7.21 (5H, m), 7.23−7.36 (4H, m). ^{13}C NMR: δ 19.42 (q), 36.86 (t), 126.06 (d), 126.06 (d), 126.40 (d), 127.02 (d), 128.46 (d), 128.50 (d), 129.22 (d), 130.22 (d), 130.92 (d), 136.38 (s), 137.58 (s), 138.24 (s).

Alkylation of Toluene with *trans*-Crotyl Chloride (3). 1-(4-Methylphenyl)-2-butene (4-p). ^{1}H NMR: δ 1.66 (3H, dq, J = 6.16, 1.30), 2.30 (3H, s), 3.26 (2H, br d, J = 5.55), 5.35−5.63 (2H, m), 7.04−7.11 (4H, m). ^{13}C NMR: δ 17.83 (q), 20.95 (q), 38.63 (t), 126.00 (d), 128.34 (d), 129.01 (d), 130.36 (d), 135.25 (s), 137.98 (s).

1-(2-Methylphenyl)-2-butene (4-o). ^{1}H NMR: δ 1.66 (3H, dq, J = 6.19, 1.38), 2.28 (3H, s), 3.29 (2H, dt, J = 6.24, 1.30), 5.42 (1H, dtq, J = 15.16, 1.38, 6.24), 5.56 (1H, dtq, J = 15.16, 6.27, 1.41), 7.08−7.15 (4H, m). ^{13}C NMR: δ 17.83 (q), 19.28 (q), 36.51 (t), 125.94 (d), 126.06 (d), 126.11 (d), 128.95 (d), 129.17 (d), 130.05 (d), 136.15 (s), 139.07 (s).

1-(2-Methylphenyl)-1-(4-methylphenyl)butane (20-op). ^{1}H NMR: δ 0.91 (3H, t, J = 7.33), 1.20−1.38 (2H, m), 1.96 (2H, dt, J = 5.29, 7.67), 2.25 (3H, s), 2.27 (2H, s), 4.06 (1H, t, J = 7.69), 7.01−7.20 (8H, m). ^{13}C NMR: δ 14.14 (q), 19.88 (q), 20.94 (q), 21.20 (t), 38.55 (t), 46.28 (d), 125.80 (d), 125.94 (d), 126.62 (d), 128.06 (d), 128.92 (d), 130.41 (d), 135.19 (s), 136.20 (s), 141.91 (s), 143.24 (s).

1,1-Bis(4-methylphenyl)butane (20-pp). ^{1}H NMR: δ 0.90 (3H, t, J = 7.30), 1.20−1.38 (2H, m), 2.00 (2H, dt, J = 5.51, 7.75), 2.27 (6H, s), 3.83 (1H, t, J = 7.81), 7.05 (4H, d, J

= 8.20), 7.10 (4H, d, J = 8.30). ^{13}C NMR: δ 14.07 (q), 20.94 (q), 21.20 (t), 38.05 (t), 50.27 (d), 127.68 (d), 129.02 (d), 135.27 (s), 142.63 (s).

1-(2-Methylphenyl)-1-butene (32-o). ^{1}H NMR: δ 1.10 (3H, t, J = 7.47), 2.22−2.25 (2H, m), 2.33 (3H, s), 6.13 (1H, dt, J = 15.68, 6.51), 6.56 (1H, dt, J = 15.62, 1.52), 7.08−7.15 (4H, m). ^{13}C NMR: δ 13.81 (q), 19.77 (q), 26.37 (t), 125.45 (d), 125.97 (d), 126.69 (d), 126.69 (d), 130.11 (d), 133.98 (d), 134.86 (s), 137.06 (s).

Alkylation of Toluene with ((4-Methylbenzenesulfonyl)oxy)cyclohexane (10). ((4-Methylbenzenesulfonyl)oxy)-cyclohexane (10). ^{1}H NMR: 1.16−1.36 (3H, m), 1.40−1.59 (3H, m), 1.60−1.82 (4H, m), 2.44 (3H, s), 4.50 (1H, tt, J = 3.72, 5.12), 7.33 (2H, d, J = 8.02), 7.79 (2H, d, J = 8.30). ^{13}C NMR: δ 21.50 (q), 23.29 (t), 24.79 (t), 32.26 (t), 81.55 (d), 127.47 (d), 129.63 (d), 134.84 (s), 144.22 (s).

Alkylation of Toluene with Cyclohexene (16). (4-Methylphenyl)cyclohexane (11-p). ^{1}H NMR: δ 1.15−1.45 (5H, m), 1.65−1.90 (5H, m), 2.31 (3H, s), 2.37−2.51 (1H, m), 6.90−7.20 (4H, m). ^{13}C NMR: δ 20.94 (q), 26.23 (t), 26.98 (t), 34.60 (t), 44.19 (d), 126.66 (d), 128.94 (d), 135.12 (s), 145.12 (s).

(2-Methylphenyl)cyclohexane (11-o). ^{1}H NMR: δ 1.15−1.45 (5H, m), 1.65−1.90 (5H, m), 2.32 (3H, s), 2.62−2.74 (1H, m), 6.90−7.20 (4H, m). ^{13}C NMR: δ 19.29 (q), 26.38 (t), 27.21 (t), 33.70 (t), 40.16 (d), 125.34 (d), 125.43 (d), 126.07 (d), 130.17 (d), 135.05 (s), 145.86 (s).

(3-Methylphenyl)cyclohexane (11-m). ^{1}H NMR: δ 1.15−1.45 (5H, m), 1.65−1.90 (5H, m), 2.31 (3H, s), 2.37−2.51 (1H, m), 6.90−7.20 (4H, m). ^{13}C NMR: δ 21.47 (q), 26.23 (t), 26.98 (t), 34.52 (t), 44.60 (d), 123.80 (d), 126.50 (d), 127.64 (d), 128.15 (d), 137.69 (s), 148.05 (s).

Alkylation of Toluene with Cyclopentene (14). (4-Methylphenyl)cyclopentane (15-p). ^{1}H NMR: δ 1.50−1.85 (6H, m), 1.95−2.07 (2H, m), 2.30 (3H, s), 3.18 (1H, tt, J = 7.60, 9.25), 6.95−7.23 (4H, m). ^{13}C NMR: δ 19.79 (q), 25.61 (t), 34.66 (t), 45.58 (d), 126.95 (d), 128.90 (d), 135.03 (s), 143.43 (s).

(2-Methylphenyl)cyclopentane (15-o). ^{1}H NMR: δ 1.50−1.85 (6H, m), 1.95−2.07 (2H, m), 2.34 (3H, s), 2.94 (1H, tt, J = 7.45, 9.60), 6.95−7.23 (4H, m). ^{13}C NMR: δ 20.93 (q), 25.52 (t), 33.61 (t), 41.67 (d), 125.20 (d), 125.43 (d), 126.04 (d), 130.07 (d), 135.85 (s), 144.52 (s).

(3-Methylphenyl)cyclopentane (15-m). ^{1}H NMR: δ 1.50−1.85 (6H, m), 1.95−2.07 (2H, m), 2.32 (3H, s), 2.94 (1H, tt, J = 7.45, 9.60), 6.95−7.23 (4H, m). ^{13}C NMR: δ 21.46 (q), 25.58 (t), 34.61 (t), 45.92 (d), 124.07 (d), 126.41 (d), 127.91 (d), 128.12 (d), 137.65 (s), 146.47 (s).

Alkylation of Toluene with Cycloheptene (17). (4-Methylphenyl)cycloheptane (18-p). ^{1}H NMR: δ 1.35−2.03 (12H, m), 2.30 (3H, s), 2.56−2.65 (1H, m), 6.90−7.20 (4H, m). ^{13}C NMR: δ 20.93 (q), 27.23 (t), 28.02 (t), 36.95 (t), 46.64 (d), 126.53 (d), 128.91 (d), 134.32 (s), 147.02 (s).

(2-Methylphenyl)cycloheptane (18-o). ^{1}H NMR: δ 1.35−2.03 (12H, m), 2.32 (3H, s), 2.81−2.91 (1H, m), 6.90−7.20 (4H, m). ^{13}C NMR: δ 19.45 (q), 27.72 (t), 27.91 (t), 36.05 (t), 41.82 (d), 125.19 (d), 125.58 (d), 126.13 (d), 130.07 (d), 134.82 (s), 148.02 (s).

(3-Methylphenyl)cycloheptane (18-m). ^{1}H NMR: δ 1.35−2.03 (12H, m), 2.31 (3H, s), 2.56−2.65 (1H, m), 6.90−7.20 (4H, m). ^{13}C NMR: δ 21.47 (q), 27.30 (t), 28.02 (t), 36.86 (t), 47.04 (d), 123.65 (d), 126.23 (d), 127.51 (d), 128.18 (d), 137.69 (s), 149.97 (s).

Alkylation of Toluene with Bromodiphenylmethane (5). (4-Methylphenyl)diphenylmethane (6-p). ^{1}H NMR: δ 2.31 (3H, s), 5.50 (1H, s), 7.00 (2H, d, J = 8.06), 7.02−7.30 (12H, m). ^{13}C NMR: δ 20.97 (q), 56.50 (d), 126.17 (d), 128.22 (d), 128.98 (d), 129.30 (d), 129.39 (d), 135.70 (s), 140.94 (s), 144.10 (s).

(2-Methylphenyl)diphenylmethane (6-o). ^{1}H NMR: δ 2.21 (3H, s), 5.67 (1H, s), 7.02−7.30 (14H, m). ^{13}C NMR: δ 19.87 (q), 53.55 (d), 125.74 (d), 126.17 (d), 126.35 (d), 128.22 (d), 129.41 (d), 129.58 (d), 130.37 (d), 136.53 (s), 142.31 (s), 143.38 (s).

Alkylation of Toluene with *trans*-1,2-Diphenylethene (30; *trans*-Stilbene). 1-(4-Methylphenyl)-1,2-diphenylethane (31-p). ^{1}H NMR: δ 2.55 (3H, s), 3.32 (2H, d, J = 7.81), 4.18 (1H, t, J = 7.76), 6.92−7.26 (14H, m). ^{13}C NMR: δ 20.96 (q), 42.15 (t), 52.66 (d), 125.80 (d), 126.05 (d), 127.86 (d), 127.99 (d), 128.26 (d), 129.02 (d), 135.57 (s), 140.37 (s), 141.47 (s), 144.72 (s).

Alkylation of Toluene with 9-Bromofluorene (7). 9-(4-Methylphenyl)fluorene (8-p). ^{1}H NMR: δ 2.30 (3H, s), 5.00 (1H, s), 6.97 (2H, d, J = 7.30), 7.07 (2H, d, J = 7.78), 7.20−7.40 (6H, m), 7.78 (2H, d, J = 7.60). ^{13}C NMR: δ 21.05 (q), 54.09 (d), 119.80 (d), 125.27 (d), 127.20 (d), 127.25 (d), 128.17 (d), 129.37 (d), 136.34 (s), 138.50 (s), 140.96 (s), 148.08 (s).

Alkylation of Toluene with (Benzenesulfonyloxy)-2-methylcyclohexane and 2-Methyl-((4-methylbenzenesulfonyl)oxy)cyclohexane (21). (Benzenesulfonyloxy)-2-methylcyclohexane. ^{1}H NMR: δ 0.79 (3H, d, J = 6.53 Hz), 0.92−1.07 (1H, m), 1.09−1.32 (2H, m), 1.37−1.52 (1H, m), 1.52−1.65 (2H, m), 1.67−1.79 (2H, m), 1.96−2.04 (1H, m), 4.15 (1H, dt, J = 4.37, 10.23), 7.54 (2H, ddt, J = 8.38, 7.40, 1.44), 7.63 (1H, tt, J = 7.40, 1.38), 7.93 (2H, dt, 8.37, 1.44). ^{13}C NMR: δ 18.33 (q), 24.63 (t), 24.73 (t), 32.73 (t), 33.40 (t), 37.53 (d), 88.22 (d), 127.59 (d), 128.99 (d), 133.31 (d), 137.85 (s).

2-Methyl-((4-methylbenzenesulfonyl)oxy)cyclohexane (21). ^{1}H NMR: δ 0.80 (3H, d, J = 6.51), 0.92−1.07 (1H, m), 1.08−1.31 (2H, m), 1.35−1.49 (1H, m), 1.49−1.61 (2H, m), 1.63−1.78 (2H, m), 1.94−2.03 (1H, m), 2.44 (3H, s), 4.11 (1H, dt, J = 4.39, 10.25), 7.32 (2H, d, J = 7.95), 7.79 (2H, d, J = 8.33). ^{13}C NMR: δ 18.34 (q), 21.52 (q), 24.60 (t), 24.72 (t), 32.66 (t), 33.38 (t), 37.52 (d), 87.86 (d), 127.59 (d), 129.57 (d), 134.85 (s), 144.23 (s).

1-Methyl-1-(4-methylphenyl)cyclohexane (22-p). ^{1}H NMR: δ 1.16 (3H, s), 1.34−1.59 (8H, m), 1.98 (2H, dd, J = 7.49, 13.00), 3.31 (3H, s), 7.12 (2H, d, J = 8.03), 7.23 (2H, d, 7.30). ^{13}C NMR: δ 20.80 (q), 22.70 (t), 26.43 (t), 30.55 (q), 37.54 (s), 37.98 (t), 125.73 (d), 128.89 (d), 134.53 (s), 147.00 (s).

Alkylation of Toluene with 2-Bicyclo[2.2.1]heptene [19; *exo*-2-Norbornene] or 2-((4-Methylbenzenesulfonyl)oxy)bicyclo[2.2.1]heptane [12; 2-Tosylnorbornane]. *exo*-2-((4-Methylbenzenesulfonyl)oxy)bicyclo[2.2.1]-heptane [2-(Tosyloxy)norbornane, 12]. ^{1}H NMR: 0.92−1.04 (2H, m), 1.10−1.17 (1H, m), 1.30−1.62 (5H, m), 2.21−2.27 (1H, m), 2.31−2.37 (1H, m), 2.43 (3H, s), 4.43 (1H, m), 7.33 (2H, d, J = 8.74), 7.77 (2H, d, J = 8.35). ^{13}C NMR: δ 21.34 (q), 23.67 (t), 27.64 (t), 34.75 (t), 35.09 (d), 39.40 (t), 41.85 (d), 85.13 (d), 127.36 (d), 129.56 (d), 134.44 (s), 144.20 (s).

2-(4-Methylphenyl)bicyclo[2.2.1]heptane (13-p). ^{1}H NMR: 1.12−1.41 (3H, m), 1.48−1.84 (5H, m), 2.24−2.41 (2H, m), 2.30 (3H, s), 2.70 (1H, dd, J = 5.93, 8.42), 7.05 (2H, d, J = 8.06), 7.23 (2H, d, J = 7.57). ^{13}C NMR: δ 20.87 (q), 28.93 (t), 30.57 (t), 36.00 (t), 36.80 (d), 39.09 (t), 43.06 (d), 46.93 (d), 126.93 (d), 128.84 (d), 134.71 (s), 144.58 (s).

2-(2-Methylphenyl)bicyclo[2.2.1]heptane (13-o). ^{1}H NMR: δ 1.12−1.41 (3H, m), 1.48−1.84 (5H, m), 2.24−2.41 (2H, m), 2.33 (3H, s), 2.80 (1H, dd, J = 5.71, 8.45), 6.93−7.25 (4H, m). ^{13}C NMR: δ 20.05 (q), 29.13 (t), 30.54 (t), 36.34 (t), 36.91 (d), 38.70 (t), 41.47 (d), 43.87 (d), 124.70 (d), 125.20 (d), 125.62 (d), 130.20 (d), 136.13 (s), 145.46 (s).

2-(3-Methylphenyl)bicyclo[2.2.1]heptane (13-m). ^{1}H NMR: δ 1.12−1.41 (3H, m), 1.48−1.84 (5H, m), 2.24−2.41 (2H, m), 2.30 (3H, s), 2.70 (1H, dd, J = 5.93, 8.42), 6.93−7.25 (4H, m). ^{13}C NMR: δ 21.52 (q), 28.93 (t), 30.62 (t), 36.09 (t), 36.80 (d), 39.09 (t), 42.93 (d), 47.26 (d), 124.00 (d), 126.07 (d), 127.94 (d), 128.06 (d), 137.60 (s), 147.55 (s).

Alkylation of Toluene with 2-(Benzenesulfonyloxy)-4-methylpentane and 4-Methyl-2-((4-methylbenzenesulfonyl)oxy)pentane (23). 2-(Benzenesulfonyloxy)-4-methylpentane. ^{1}H NMR: δ 0.91 (3H, d, J = 6.55), 0.92 (3H, d, J = 6.59), 1.19 (3H, d, J = 6.16), 1.26 (1H, dd, J = 5.00, 13.21), 1.41 (1H, ddd, J = 5.95, 8.16, 13.78), 1.74 (1H, dhep, J = 5.62, 6.57), 3.88 (1H, ddq, J = 5.00, 8.16, 6.13), 7.63 (2H, ddm, J = 7.33, 8.03), 7.76 (1H, tt, J = 7.45, 1.25), 8.05 (2H, dt, 8.60, 1.30). ^{13}C NMR: δ 22.29 (q), 23.12 (q), 23.97 (q), 24.79 (d), 48.62 (t), 66.12 (d), 126.91 (d), 129.65 (d), 135.19 (d), 144.41 (s).

4-Methyl-2-((4-methylbenzenesulfonyl)oxy)pentane (23). ^{1}H NMR: δ 0.76 (3H, d, J = 6.54), 0.82 (3H, d, J = 6.37), 1.26 (3H, d, J = 6.24), 1.16−1.34 (1H, m), 1.45−1.64 (2H, m), 2.44 (3H, s), 4.68 (1H, ddq, J = 5.15, 7.84, 6.24), 7.33 (2H, d, J = 7.98), 7.79 (2H, d, J = 8.31). ^{13}C NMR: δ 21.20 (q), 21.48 (q), 21.89 (q), 22.62 (q), 24.22 (d), 45.78 (t), 79.01 (d), 127.61 (d), 129.61 (d), 134.72 (d), 144.29 (s).

2-Methyl-2-(4-methylphenyl)pentane (24-p). ^{1}H NMR: δ 0.81 (3H, t, J = 7.2), 1.00−1.15 (2H, m), 1.27 (6H, s), 1.50−1.59 (2H, m), 2.30 (3H, s), 7.09 (2H, d, J = 7.97), 7.21 (2H, d, J = 8.33). ^{13}C NMR: δ 14.77 (q), 18.01 (t), 20.81 (q), 29.01 (q), 37.38 (s), 41.15 (t), 125.68 (d), 128.66 (d), 134.56 (s), 146.79 (s).

2-Methyl-2-(3-methylphenyl)pentane (24-m). ^{1}H NMR: δ 0.81 (3H, t, J = 7.23), 1.00−1.15 (2H, m), 1.27 (6H, s), 1.50−1.59 (2H, m), 2.30 (3H, s), 7.05−7.25 (4H, m). ^{13}C NMR: δ 14.77 (q), 18.01 (t), 21.21 (q), 29.07 (q), 37.39 (s), 41.15 (t), 122.85 (d), 126.00 (d), 126.57 (d), 127.82 (d), 137.26 (s), 149.86 (s).

3-Methyl-3-(4-methylphenyl)pentane (25-p). ^{1}H NMR: δ 0.66 (6H, t, J = 7.45), 1.16−1.25 (4H, m), 1.27 (3H, s), 2.34 (3H, s), 7.09 (2H, d, J = 7.97), 7.16 (2H, d, J = 8.11). ^{13}C NMR: δ 8.67 (q), 20.81 (q), 23.00 (q), 35.09 (t), 40.71 (s), 126.47 (d), 128.59 (d), 134.37 (s), 144.53 (s).

Alkylation of Toluene with 2-Chloro-2-methylpropane (*tert*-Butyl Chloride). 2-Methyl-2-(4-methylphenyl)propane (9-p). ^{1}H NMR: δ 1.30 (9H, s), 2.30 (3H, s), 7.10 (2H,d m, J = 7.95), 7.27 (2H, d, J = 8.30). ^{13}C NMR: δ 20.83 (q), 31.45 (q), 34.31 (s), 125.13 (d), 128.76 (d), 134.76 (s), 148.16 (s).

2-Methyl-2-(3-methylphenyl)propane (9-m). ^{1}H NMR: δ 1.31 (9H, s), 2.34 (3H, s), 7.05−7.30 (4H, m). ^{13}C NMR: δ 20.85 (q), 31.41 (q), 34.35 (s), 122.29 (d), 126.05 (d), 126.17 (d), 127.98 (d), 137.47 (s), 151.17 (s).

Reaction of Toluene with Ethyl 2-((4-Methylbenzenesulfonyl}oxy)propanoate. Ethyl 2-Hydroxypropanoate (Ethyl Lactate). ^{1}H NMR: δ 1.30 (3H, t, J = 7.13), 1.42 (3H, d, J = 6.94), 2.98 (1H, br s), 4.24 (2H, q, J = 7.14), 4.27 (1H, q, J = 6.92). ^{13}C NMR: δ 14.00 (q), 20.21 (q), 61.41 (t), 66.67 (d), 175.56 (s).

Ethyl 2-((4-Methylbenzenesulfonyl)oxy)propanoate. ^{1}H NMR: δ 1.21 (3H, t, J = 7.14), 1.51 (3H, d, J = 6.94), 2.45 (3H, s), 4.12 (2H, q, J = 7.16), 4.93 (1H, q, J = 6.95), 7.34 (2H, d, J = 8.00), 7.82 (2H, d, J = 8.36). ^{13}C NMR: δ 13.83 (q), 18.29 (q), 21.53 (q), 61.68 (t), 74.10 (d), 127.91 (d), 129.68 (d), 133.44 (s), 144.94 (s), 168.91 (s).

2-((4-Methylbenzenesulfonyl)oxy)propanoic Acid. ^{1}H NMR: δ 1.54 (3H, d, J = 7.00), 2.45 (3H, s), 4.97 (1H, q, J = 7.00), 7.35 (2H, d, J = 7.97), 7.82 (2H, d, J = 8.31), 9.45−9.70 (1H, br s). ^{13}C NMR: δ 18.19 (q), 21.58 (q), 73.21 (d), 127.92 (d), 129.84 (d), 133.11 (s), 145.28 (s), 174.01 (s).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of many compounds (49 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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