California—San Francisco, supported by the NIH Division of Research Resources.

Registry No. 1, 56407-82-0; **2a**, 57795-10-5; **2b**, 115843-67-9; **3**, 137871-60-4; **4**, 137871-61-5; **5**, 137871-62-6; **6**, 137871-63-7; (*R**,*R**)-**7**, 137871-64-8; (*R**,*R**)-**7** alcohol, 137871-70-6; (*R**,*S**)-**7**, 137871-77-3; (*R**,*S**)-**7** alcohol, 137871-76-2; (*R**,*R**)-**8**, 137871-65-9; (*R**,*S**)-**8**, 137871-78-4; **9**, 24157-02-6; **10**, 137871-66-0; **11a**, 137871-92-2; **11b**, 137871-91-1; **12**, 137871-67-1; **13**, 137871-68-2; **14**, 137871-69-3; **15**, 137871-93-3; **16**, 137871-94-4; **17**, 137871-71-7; **18**, 137871-72-8; **19**, 137871-73-9; **20**, 137871-74-0; **21**, 137871-75-1; **22** (*n* = 1), 137871-96-6; **22** (*n* = 3), 137871-95-5; **23** (*n* = 1), 137871-97-7; **23** (*n* = 3), 137871-97-7; **24** (*n* = 1), 137872-00-5; **24** (*n* = 3), 137871-99-9; **25** (*n* = 1), 137872-02-7; **25** (*n* = 3), 137872-01-6; **26** (*n* = 1), 137872-04-9; **26** (*n* = 3), 137872-03-8; **27**, 137871-79-5; **28**, 137871-80-8; **29**, 137871-81-9; **30**, 137871-82-0; **31**, 137871-83-1; **32**, 137871-84-2; **35**, 137871-85-3; **36**, 137871-86-4; **37**, 137871-87-5; **38**, 137871-88-6; **39**, 137871-89-7; **40**, 137871-90-0; diethyl (phenylsulfonyl)methane phosphonate, 56069-39-7; [(4-chlorophenyl)sulfinyl]methyl phenyl sulfone, 133445-41-7; *tert*-butyldimethylsilyl triflate, 69739-34-0; bis(methylthio)methane, 1618-26-4; tetrahydrofuran, 109-99-9; 2-methyltetrahydropyran, 10141-72-7; 1,3-propanedithiol, 109-80-8; 2-bromo-3-(trimethylsilyl)propene, 81790-10-5; 2-acetyl-1,3-dithiane, 58277-26-2; 4-iodobutanal dimethyl acetal, 91988-32-8; 5-(*tert*-butyldimethylsiloxy)-1-bromopentane, 85514-43-8; 3-(*tert*-butyldimethylsiloxy)-1-bromopropane, 89031-84-5; palladium acetate, 3375-31-3; triisopropyl phosphite, 116-17-6; trimethylenemethane, 13001-05-3.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for all compounds lacking a combustion analysis and experimental procedures for **2a**, **2b**, **9**, **15**, **16**, 2-acetyl-1,3-dithiane, 4,4-dimethoxy-1-iodobutane, **17**, 3-(*tert*-butyldimethylsiloxy)-1-bromopropane, and 5-(*tert*-butyldimethylsiloxy)-1-bromopentane (33 pages). Ordering information is given on any current masthead page.

Sulfonylation of Organometallic Reagents with Arenesulfonyl Fluorides: A Simple One-Step Synthesis of Sulfones

Leah L. Frye,* Eileen L. Sullivan, Kevin P. Cusack, and John M. Funaro

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12180-3590

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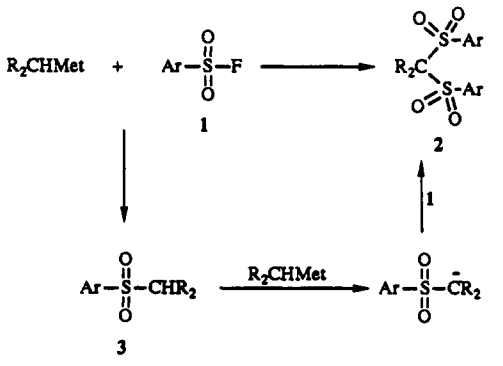
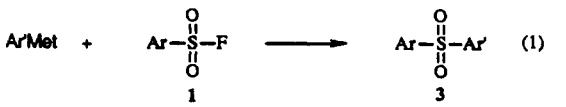
Sulfonylation of organometallic reagents was accomplished with arenesulfonyl fluorides to provide a wide variety of alkylaryl- and diaryl sulfones. Organolithium and diorganocopper lithium reagents react smoothly with arenesulfonyl fluorides to give sulfones in high yields. Alkyl Grignard reagents often lead to mixtures of monosulfonylated and disulfonylated products. However, allylmagnesium chloride and phenylmagnesium chloride provide the corresponding sulfones in excellent yields. Organocopper reagents were also found to yield sulfones upon treatment with arenesulfonyl fluorides. By utilizing this methodology, synthetically useful alkyl, (trimethylsilyl)methyl, and allyl sulfones are easily prepared in high yields.

Sulfones are of interest as intermediates in organic synthesis[1] and as pharmaceutical agents.[2] Common methods for the preparation of sulfones include oxidation of sulfides and sulfoxides, Friedel–Crafts sulfonylation of aromatic hydrocarbons, and alkylation of sulfinates.[1] Examples of the direct sulfonylation of organometallic reagents are rare.[3-7] A limited number of examples exist

Scheme I



in which *aryl* organometallic reagents (Ar'Met) are successfully sulfonylated with sulfonyl fluorides (eq 1).[6,8,9]



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0022-3263/92/1957-0697$03.00/0

Table I. Sulfonylation of Organometallic Reagents with $ArSO_2F$

RMet + $ArSO_2F$ → monosulfone + disulfone
1 3 2

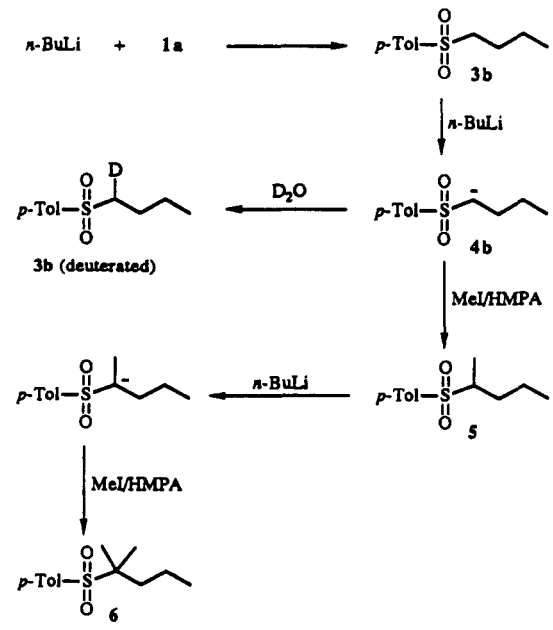
entry	Ar	organometallic reagent (RMet)	monosulfone (% yield)[a]	disulfone (% yield)[a]
1	*p*-Tol	MeLi	**3a**: *p*-$TolSO_2Me$ (94)	**2a**: $(p\text{-}TolSO_2)_2CH_2$ (0)
2	*p*-Tol	*n*-BuLi	**3b**: *p*-$TolSO_2$-*n*-Bu (92)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
3	*p*-Tol	$TMSCH_2Li$	**3c**: *p*-$TolSO_2CH_2TMS$ (70)	**2c**: $(p\text{-}TolSO_2)_2CHTMS$ (0)
4	*p*-Tol	*s*-BuLi	**3d**: *p*-$TolSO_2$-*s*-Bu (91)	**2d**: $(p\text{-}TolSO_2)_2C(CH_3)CH_2CH_3$ (0)
5	*p*-Tol	*t*-BuLi	**3e**: *p*-$TolSO_2$-*t*-Bu (94)	
6	*p*-Tol	PhLi	**3f**: *p*-$TolSO_2Ph$ (76)	
7	Ph	PhLi	**3g**: $PhSO_2Ph$ (67)	
8	*p*-Tol	Ph_3CLi	**3h**: *p*-$TolSO_2CPh_3$ (0)	
9	*p*-Tol	TMSC≡CLi	**3i**: *p*-$TolSO_2C{\equiv}CH$ (8)	
10	*p*-Tol	MeMgCl	**3a**: *p*-$TolSO_2Me$ (87)	**2a**: $(p\text{-}TolSO_2)_2CH_2$ (8)
11	*p*-Tol	*n*-BuMgCl[b]	**3b**: *p*-$TolSO_2$-*n*-Bu (0)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
12	*p*-Tol	*n*-BuMgCl[c]	**3b**: *p*-$TolSO_2$-*n*-Bu (59)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (16)
13	*p*-Tol	*n*-BuMgCl[d]	**3b**: *p*-$TolSO_2$-*n*-Bu (26)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (32)
14	*p*-Tol	PhMgBr	**3f**: *p*-$TolSO_2Ph$ (95)	
15	Ph	PhMgBr	**3g**: $PhSO_2Ph$ (95)	
16	*p*-Tol	HC≡CMgBr	**3i**: *p*-$TolSO_2C{\equiv}CH$ (12)	
17	*p*-Tol	$cycloC_6H_{11}MgCl$	**3j**: *p*-$TolSO_2cycloC_6H_{11}$ (32)	**2j**: $(p\text{-}TolSO_2)_2cycloC_6H_{10}$ (0)
18	*p*-Tol	*i*-BuMgCl	**3k**: *p*-$TolSO_2$-*i*-Bu (13)	**2k**: $(p\text{-}TolSO_2)_2CHCH(CH_3)_2$ (18)
19	*p*-Tol	allylMgCl	**3l**: *p*-$TolSO_2CH_2CH{=}CH_2$ (99)	**2l**: $(p\text{-}TolSO_2)_2CHCH{=}CH_2$ (0)
20	*p*-Tol	vinylMgBr	**3m**: *p*-$TolSO_2CH{=}CH_2$ (0)	
21	*p*-Tol	Me_2CuLi	**3a**: *p*-$TolSO_2Me$ (71)	**2a**: $(p\text{-}TolSO_2)_2CH_2$ (0)
22	*p*-Tol	$n\text{-}Bu_2CuLi$	**3b**: *p*-$TolSO_2$-*n*-Bu (99)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
23	*p*-Tol	$(TMSCH_2)_2CuLi$	**3c**: *p*-$TolSO_2CH_2TMS$ (49)[e]	**2c**: $(p\text{-}TolSO_2)_2CHTMS$ (0)
24	*p*-Tol	$s\text{-}Bu_2CuLi$	**3d**: *p*-$TolSO_2$-*s*-Bu (83)	**2d**: $(p\text{-}TolSO_2)_2C(CH_3)CH_2CH_3$ (0)
25	*p*-Tol	$t\text{-}Bu_2CuLi$	**3e**: *p*-$TolSO_2$-*t*-Bu (69)	
26	*p*-Tol	Ph_2CuLi	**3f**: *p*-$TolSO_2Ph$ (84)	
27	*p*-Tol	*n*-BuCuSPhLi	**3b**: *p*-$TolSO_2$-*n*-Bu (12)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (3)
28	*p*-Tol	$Me_2CuMgCl$	**3a**: *PtOLso*$_2$mE (29)	**2A**: $(PtOLso_2)_2ch_2$ (10)
29	*p*-Tol	$n\text{-}Bu_2CuMgCl$	**3b**: *p*-$TolSO_2$-*n*-Bu (8)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
30	*p*-Tol	$Ph_2CuMgBr$	**3f**: *p*-$TolSO_2Ph$ (79)	
31	*p*-Tol	$(cycloC_6H_{11})_2CuMgCl$	**3j**: *p*-$TolSO_2cycloC_6H_{11}$ (0)	**2j**: $(p\text{-}TolSO_2)_2cycloC_6H_{10}$ (0)
32	*p*-Tol	$i\text{-}Bu_2CuMgCl$	**3k**: *p*-$TolSO_2$-*i*-Bu (0)	**2k**: $(p\text{-}TolSO_2)_2CHCH(CH_3)_2$ (0)
33	*p*-Tol	$(allyl)_2CuMgCl$	**3l**: *p*-$TolSO_2CH_2CH{=}CH_2$ (86)	**2l**: $(p\text{-}TolSO_2)_2CHCH{=}CH_2$ (0)
34	*p*-Tol	*n*-BuPhSCuMgCl	**3b**: *p*-$TolSO_2$-*n*-Bu (0)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
35	*p*-Tol	MeCu[f]	**3a**: *p*-$TolSO_2Me$ (86)	**2a**: $(p\text{-}TolSO_2)_2CH_2$ (0)
36	*p*-Tol	*n*-BuCu[f]	**3b**: *p*-$TolSO_2$-*n*-Bu (88)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
37	*p*-Tol	*s*-BuCu[f]	**3d**: *p*-$TolSO_2$-*s*-Bu (34)	**2d**: $(p\text{-}TolSO_2)_2C(CH_3)CH_2CH_3$ (0)
38	*p*-Tol	*t*-BuCu[f]	**3e**: *p*-$TolSO_2$-*t*-Bu (17)	
39	*p*-Tol	PhCu[f]	**3f**: *p*-$TolSO_2Ph$ (94)	
40	*p*-Tol	allylCu[g]	**3l**: *p*-$TolSO_2CH_2CH{=}CH_2$ (20)	**2l**: $(p\text{-}TolSO_2)_2CHCH{=}CH_2$ (0)
41	*p*-Tol	*n*-BuCuP(*n*-Bu)$_3$[f]	**3b**: *p*-$TolSO_2$-*n*-Bu (0)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)
42	*p*-Tol	*n*-BuCuP(*n*-Bu)$_3$[g]	**3b**: *p*-$TolSO_2$-*n*-Bu (0)	**2b**: $(p\text{-}TolSO_2)_2CH\text{-}n\text{-}C_3H_7$ (0)

[a] Isolated yields. [b] Reaction performed at −78 °C. [c] Reaction performed at 0 °C. [d] Reaction performed at 25 °C. [e] Also isolated methyl *p*-tolyl sulfone (**3a**, 28%). [f] Prepared from the corresponding organolithium reagents. [g] Prepared from the corresponding Grignard reagent.

However, all reported reactions between *alkyl* organometallic reagents and arenesulfonyl fluorides **1** result in the formation of β-disulfones **2** via formation of monosulfone **3** followed by α-deprotonation and reaction with another molecule of sulfonyl fluoride **1** to give disulfone **2** (Scheme I).[10] Our interest in sulfones prompted us to study this reaction further in the hopes of developing a new general method for the preparation of a variety of synthetically useful alkyl aryl sulfones.

As can be seen in Table I, the addition of alkyl- and aryllithium reagents to arenesulfonyl fluorides **1** at −78 °C results in the formation of alkyl aryl and diaryl sulfones **3** in high yields (Table I, entries 1–7). In the case of

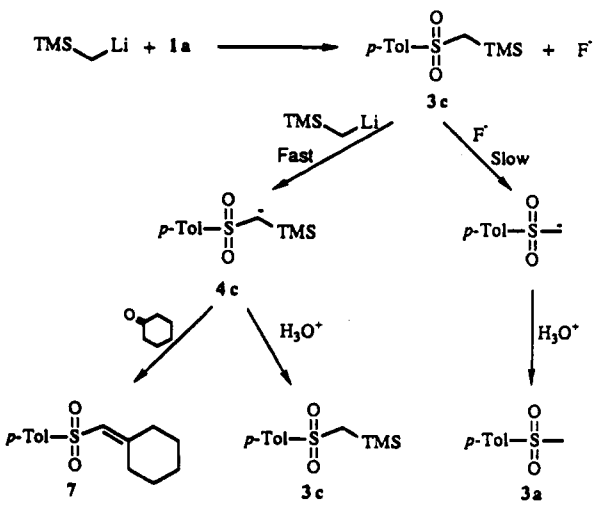
Scheme II



(9) Numerous examples of reactions between arenesulfonyl fluorides and stabilized anions exist. For representative examples, see: (a) Pigou, P. E.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1988**, 725–730. (b) van Leusen, A. M.; Boerma, G. J. M.; Helmholdt, R. B.; Siderius, H.; Strating, J. *Tetrahedron Lett.* **1972**, 2367–2368. (c) Schollkopf, U.; Schroder, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 311–312. (d) van Leusen, A. M.; Reith, B. A.; Iedema, A. J. W.; Strating, J. *Rec. Trav. Chim.* **1972**, *91*, 37–49. (e) Hirsch, E.; Hunig, S.; Reibig, H.-U. *Chem. Ber.* **1982**, *115*, 3687–3696. (f) Hirsch, E.; Hunig, S.; Reibig, H.-U. *Chem. Ber.* **1982**, *115*, 399–401.

(10) Fukuda, H.; Frank, F. J.; Truce, W. E. *J. Org. Chem.* **1963**, *28*, 1420.

Scheme III



n-butyllithium (Table I, entry 2), optimization experiments indicated a dramatic reduction in the yield of sulfone **3b** when less than 2 equiv of *n*-butyllithium were utilized suggesting rapid α-deprotonation of sulfone **3b** to form sulfonyl-stabilized anion **4b** (Scheme II). Quenching the reaction with D_2O instead of ammonium chloride verified this hypothesis. Anion **4b** could also be alkylated with MeI/HMPA to yield either monomethylated sulfone **5** or dimethylated sulfone **6** depending upon the number of equivalents of *n*-BuLi utilized.

This methodology also lead to the preparation of (trimethylsilyl)methyl aryl sulfone **3c** (Table I, entry 3), a key intermediate in the synthesis of vinyl sulfones.[11] During the first step of this reaction 1 equiv of fluoride ion is generated. Fluoride ion is commonly used to cleave trimethylsilyl groups,[12] and yet we are able to isolate (trimethylsilyl)methyl *p*-tolyl sulfone (**3c**) in 70% yield. The desilylated product **3a** was obtained in a yield of only 5% (Scheme III). This suggests that the rate of abstraction of the α-proton is much faster than the rate of fluoride ion mediated cleavage of the trimethylsilyl group. Once the sulfonyl stabilized anion **4c** is formed, displacement of the trimethylsilyl group is inhibited (Scheme III). In support of this hypothesis, we found that treatment of *p*-toluenesulfonyl fluoride with 2 equiv of (trimethylsilyl)methyllithium followed by quenching with cyclohexanone resulted in the formation of vinyl sulfone **7** in 54% yield (Scheme III).

In contrast to the organolithium reagents, Grignard reagents with α-protons (except allylmagnesium chloride) generally react with arenesulfonyl fluorides **1** to yield mixtures of monosulfones **3** and disulfones **2** (Scheme I, $R_2CHMet = R_2CHMgX$, Table I, entries 10–15). Grignard reagents are completely unreactive toward *p*-toluenesulfonyl fluoride (**1a**) at −78 °C; at higher temperatures, reaction does occur but the distribution of products is strongly dependent upon the temperature at which the reaction is carried out (see Table I, entries 11–13). On the other hand, the phenyl aryl sulfones **3f**[13] and **3g** (Table I, entries 14 and 15), as well as synthetically useful allyl *p*-tolyl sulfone[1c] (**3l**) (Table I, entry 19), were prepared in excellent yields from their respective Grignard reagents.

The utilization of lithium diorganocuprates results in the formation of monosulfones **3** in good to excellent yields (Table I, entries 21–26). In these cases, no disulfones **2** are observed presumably due to the decreased basicity of cuprates as compared to organolithium and Grignard reagents. When the reaction of *p*-toluenesulfonyl fluoride (**1a**) with di-*n*-butylcopper lithium is quenched with D_2O, only a small amount of deuterium is incorporated into isolated sulfone **3b**. In the case using bis[(trimethylsilyl)methyl]copper lithium, the yield of (trimethylsilyl)methyl sulfone **3c** (49%, Table I, entry 23) is considerably lower than the other examples due to the formation of substantial quantities of methyl *p*-tolyl sulfone (**3a**) (28%). This is not unexpected, since cuprates are not basic enough to generate the sulfonyl-stabilized anion **4c** (Scheme III); the fluoride ion released in the reaction is thus free to mediate cleavage of the carbon–silicon bond. Magnesio cuprates, other than those formed from allyl and phenyl Grignard reagents, are much less reactive toward arenesulfonyl fluorides than the corresponding lithio cuprates (Table I, entries 28–33).

The sulfonylation of organcopper reagents with arenesulfonyl fluorides **1** was pursued based on the observation that organocopper reagents are readily acylated with acyl halides.[14] When the organocopper reagent is generated from the corresponding lithium reagent, monosulfones **3** are obtained (Table I, entries 35–39). Primary, methyl-, and arylcopper reagents provide good yields of the corresponding sulfones (Table I; entries 35, 36, and 39). However, secondary and tertiary copper reagents, having poor thermal stability,[14] result in low yields of the corresponding sulfones (Table I, entries 37 and 38). Organocopper reagents obtained from Grignard reagents and tri-*n*-butylphosphine-stabilized organocopper reagents are virtually unreactive toward arenesulfonyl fluorides **1**.

In summary, the sulfonylation of organometallic reagents with arenesulfonyl fluorides provides a new method for the preparation of a wide variety of sulfones. By utilizing this methodology, synthetically useful alkyl, (trimethylsilyl)methyl, and allyl sulfones can be prepared easily in high yields.

Experimental Section

Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl prior to use. Hexamethylphosphoramide (HMPA) was purified by distillation from calcium hydride. Methyllithium was titrated using diphenylacetic acid as an indicator. All other organometallic reagents were titrated using 1,10-phenanthroline as an indicator.[15] All reactions were carried out under a positive pressure of N_2 unless otherwise indicated. All materials were obtained from commercial suppliers and were used without purification unless otherwise indicated.

Normal Workup. The reaction was quenched with aqueous saturated NH_4Cl. The THF was removed under reduced pressure and the residue extracted with CH_2Cl_2. The combined organic layers were washed with water, dried with anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (silica gel, 10:1 hexane/diethyl ether, unless otherwise indicated).

General Procedure A: Preparation of Sulfones via Treatment of Arenesulfonyl Fluorides with Organolithium Reagents. The appropriate organolithium reagent (1.72 mmol) was added dropwise over 5 min to a rapidly stirred solution of arenesulfonyl fluoride (0.57 mmol, *p*-toluenesulfonyl fluoride unless otherwise noted) in anhydrous THF (10 mL) at −78 °C. The solution was stirred at −78 °C for the designated period of

(11) (a) Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 183–194. (b) Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 195–204. (c) Jones, P. S.; Ley, S. V.; Simpkins, N. S.; Whittle, A. J. *Tetrahedron* **1986**, *42*, 6519–6534.

(12) For an illustrative example, see: Nakamura, E.; Shimizu, M.; Kuwajima, I. *Tetrahedron Lett.* **1976**, 1699–1702.

(13) Khodair reported an 82% yield for this reaction. See ref 8b.

(14) Normant, J. F. *Synthesis* **1972**, 63–80.

(15) Watson, S.; Eastham, J. *J. Organomet. Chem.* **1967**, *9*, 165–168.

time unless otherwise stated. Normal workup was followed.

General procedure A was followed for the following reactions.

Methyl *p*-Tolyl Sulfone (3a, Table I, Entry 1). Reaction time: 20 min. Sulfone **3a** was obtained in 94% yield as a white solid: mp 85–86 °C (lit.[16] mp 87–88 °C).

***n*-Butyl *p*-Tolyl Sulfone (3b, Table I, Entry 2).** Reaction time: 20 min. Sulfone **3b** was obtained in 92% yield as a pale yellow oil: bp 135–140 °C (1 mmHg) [lit.[17] bp 137–142 °C (1 mmHg).

***p*-Tolyl (Trimethylsilyl)methyl Sulfone (3c, Table I, Entry 3).** Reaction time: 60 min. Flash chromatography solvent system: 5:1 hexanes/diethyl ether. Sulfone **3c** was obtained in 70% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.81 (d, 2 H, J = 8.2 Hz), 7.34 (d, 2 H, J = 8.2 Hz), 2.80 (s, 2 H), 2.45 (s, 3 H), 0.30 (s, 9 H).

***sec*-Butyl *p*-Tolyl Sulfone (3d, Table I, Entry 4).** Reaction time: 20 min. Sulfone **3d** was obtained in 91% yield as a pale yellow oil which was recrystallized from hexane: mp 39.5–40 °C (lit.[18] mp 41–42 °C).

***tert*-Butyl *p*-Tolyl Sulfone (3e, Table I, Entry 5).** Reaction time: 30 min. Sulfone **3e** was obtained in 94% yield as a white solid: mp 118–121 °C (lit.[19] mp 121 °C).

Phenyl *p*-Tolyl Sulfone (3f, Table I, Entry 6). Reaction conditions: 4 h at rt. Sulfone **3f** was obtained in 76% yield as a white solid: mp 126–127 °C (lit.[8b] mp 125 °C).

Diphenyl Sulfone (3g, Table I, Entry 7). Arenesulfonyl fluoride: phenylsulfonyl fluoride. Reaction conditions: 4 h at rt. Sulfone **3g** was obtained in 67% yield as a white solid: mp 127–129 °C (lit.[20] mp 129 °C).

Ethynyl *p*-Tolyl Sulfone (3i, Table I, Entry 9). Reaction conditions: 5 h at −10 °C. Flash chromatography solvent systems: 5:1 hexanes/ethyl acetate. Desilylated sulfone **3i** was obtained in 8% yield as a pale yellow oil which was recrystallized from hexane: mp 74–75 °C (lit.[21] mp 74–75 °C).

General Procedure B: Preparation of Sulfones via Treatment of Arenesulfonyl Fluorides with Grignard Reagents. The appropriate Grignard reagent (1.72 mmol) was added dropwise over 5 min to a rapidly stirred solution of arenesulfonyl fluoride (0.57 mmol, *p*-toluenesulfonyl fluoride unless otherwise noted) in anhydrous THF (10 mL) at −78 °C. The solution was allowed to warm to rt and stirred for the designated period of time. Normal workup was followed.

General procedure B was followed for the following reactions.

Methyl *p*-Tolyl Sulfone (3a, Table I, Entry 10). Reaction time: 19 h. Flash chromatography solvent system: 5:1 hexanes/ethyl acetate. Sulfone **3a** was obtained in 87% yield. Disulfone **2a** was obtained in 8% yield as a white solid: mp 130.5–131.5 °C (lit.[22] mp 134–135 °C).

***n*-Butyl *p*-Tolyl Sulfone (3b, Table I, Entry 12).** Reaction conditions: initial addition of *n*-butylmagnesium chloride was performed at 0 °C and then the reaction was stirred for 48 h at rt. Sulfone **3b** was obtained in 59% yield. Disulfone **2b** was obtained in 16% yield as a white solid: mp 101–103 °C (lit.[10] mp 102–104 °C).

Phenyl *p*-Tolyl Sulfone (3f, Table I, Entry 14). Reaction time: 4 h. Sulfone **3f** was obtained in 95% yield.

Diphenyl Sulfone (3g, Table I, Entry 15). Arenesulfonyl fluoride: phenylsulfonyl fluoride. Reaction time: 4 h. Sulfone **3g** was obtained in 95% yield.

Ethynyl *p*-Tolyl Sulfone (3i, Table I, Entry 16). Reaction time: 72 h. Sulfone **3i** was obtained in 12% yield.

Cyclohexyl *p*-Tolyl Sulfone (3j, Table I, Entry 17). Reaction time: 23 h. Sulfone **3j** was obtained in 32% yield which was recrystallized from hexane: mp 83.5–85.0 °C (lit.[23] mp 84–86 °C).

Isobutyl *p*-Tolyl Sulfone (3k, Table I, Entry 18). Reaction time: 23 h. Sulfone **3k** was obtained as a pale yellow oil in 13% yield: ^{1}H NMR ($CDCl_3$, 200 MHz, lit.[24]) δ 7.80 (d, 2 H, J = 8.0 Hz), 7.38 (d, 2 H, J = 8.0 Hz), 2.99 (d, 2 H, J = 7.2 Hz), 2.45 (s, 3 H), 2.32–2.14 (m, 1 H), 1.05 (d, 6 H, J = 7.2 Hz). Disulfone **2k** was obtained as a white solid in 18% yield: mp 107–110 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.81 (d, 4 H, J = 8.4 Hz), 7.38 (d, 4 H, J = 8.4 Hz), 4.42 (d, 1 H, J = 1.2 Hz), 2.89–2.81 (m, 1 H), 2.45 (s, 6 H), 1.29 (d, 6 H, J = 7.5 Hz).

Allyl *p*-Tolyl Sulfone (3l, Table I, Entry 19). Reaction time: 20 min. Flash chromatography solvent system: 5:1 hexanes/diethyl ether. Sulfone **3l** was obtained as a white solid in 99% yield: mp 51–52 °C (lit.[3] mp 52–53 °C).

General Procedure C: Preparation of Sulfones via Treatment of Arenesulfonyl Fluorides with Diorganocopper Lithium Reagents. The appropriate diorganocopper lithium reagent was prepared by dropwise addition of the corresponding organolithium reagent (3.44 mmol) to a rapidly stirred slurry of copper(I) iodide (1.72 mmol) in anh THF (10 mL) at −78 °C, and the resultant mixture was stirred at −78 °C for 15 min. A solution of the arenesulfonyl fluoride (0.57 mmol, *p*-toluenesulfonyl fluoride unless otherwise noted) in anhydrous THF (2 mL) was then added slowly. The mixture was allowed to warm to rt and stirred for the given period of time. Normal workup was followed.

General procedure C was followed for the following reactions:

Methyl *p*-Tolyl Sulfone (3a, Table I, Entry 21). Reaction time: 18 h. Sulfone **3a** was obtained in 71% yield.

***n*-Butyl *p*-Tolyl Sulfone (3b, Table I, Entry 22).** Reaction time: 18 h. Sulfone **3b** was obtained in 99% yield.

***p*-Tolyl (Trimethylsilyl)methyl Sulfone (3c, Table I, Entry 23).** Reaction time: 6 h. Sulfone **3c** was obtained in 49% yield along with desilylated sulfone **3a** in 28% yield.

***sec*-Butyl *p*-Tolyl Sulfone (3d, Table I, Entry 24).** Reaction time: 42 h. Sulfone **3d** was obtained in 83% yield.

***tert*-Butyl *p*-Tolyl Sulfone (3e, Table I, Entry 25).** Reaction time: 18 h. Sulfone **3e** was obtained in 69% yield.

Phenyl *p*-Tolyl Sulfone (3f, Table I, Entry 26). Reaction time: 4 h. Sulfone **3f** was obtained in 84% yield.

General Procedure D: Preparation of Sulfones via Treatment of Arenesulfonyl Fluorides with Diorganocopper Magnesium Halide Reagents. The appropriate diorganocopper magnesium halide reagent was prepared by dropwise addition of the corresponding Grignard reagent (3.44 mmol) to a rapidly stirred slurry of copper(I) iodide (1.72 mmol) in anhydrous THF (10 mL) at −78 °C, and the resultant mixture was stirred at −78 °C for 15 min. A solution of the arenesulfonyl fluoride (0.57 mmol, *p*-toluenesulfonyl fluoride unless otherwise noted) in anhydrous THF (2 mL) was then added slowly. The mixture was allowed to warm to rt and stirred for the given period of time. Normal workup was followed.

General procedure D was followed for the following reactions:

Methyl-*p*-Tolyl Sulfone (3a, Table I, Entry 28). Reaction time: 18 h. Flash chromatography solvent system: 5:1 hexanes/ethyl acetate. Sulfone **3a** was obtained in 29% yield along with disulfone **2a** in 10% yield.

***n*-Butyl *p*-Tolyl Sulfone (3b, Table I, Entry 29).** Reaction time: 27 h. Sulfone **3b** was obtained in 8% yield.

Phenyl *p*-Tolyl Sulfone (3f, Table I, Entry 30). Reaction time: 48 h. Sulfone **3f** was obtained in 79% yield.

Allyl *p*-Tolyl Sulfone (3l, Table I, Entry 33). Reaction time: 4 h. Sulfone **3l** was obtained in 86% yield.

General Procedure E: Preparation of Sulfones via Treatment of Arenesulfonyl Fluorides with Organocopper Reagents. The appropriate organocopper reagent was prepared by dropwise addition of the corresponding organolithium reagent (1.72 mmol) to a rapidly stirred slurry of copper(I) iodide (1.72 mmol) in anhydrous THF (10 mL) at −78 °C, and the resultant

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mixture was stirred at -78 °C for 15 min. A solution of the arenesulfonyl fluoride (0.57 mmol, *p*-toluenesulfonyl fluoride unless otherwise noted) in anhydrous THF (2 mL) was then added slowly. The mixture was allowed to warm to rt and stirred for the given period of time. Normal workup was followed.

General procedure E was followed for the following reactions.

Methyl *p*-Tolyl Sulfone (3a, Table I, Entry 35). Reaction time: 18 h. Sulfone **3a** was obtained in 86% yield.

***n*-Butyl *p*-Tolyl Sulfone (3b, Table I, Entry 36).** Reaction time: 18 h. Sulfone **3b** was obtained in 88% yield.

***sec*-Butyl *p*-Tolyl Sulfone (3d, Table I, Entry 37).** Reaction time: 36 h. Sulfone **3d** was obtained in 34% yield.

***tert*-Butyl *p*-Tolyl Sulfone (3e, Table I, Entry 38).** Reaction time: 18 h. Sulfone **3e** was obtained in 17% yield.

Phenyl *p*-Tolyl Sulfone (3f, Table I, Entry 39). Reaction time: 24 h. Sulfone **3f** was obtained in 94% yield.

Preparation of 2-Pentyl *p*-Tolyl Sulfone (5) via Treatment of *p*-Toluenesulfonyl Fluoride (1a) with *n*-BuLi (2 equiv) Followed by Methyl Iodide. *n*-Butyllithium (0.60 mL, 1.21 mmol) was added dropwise over 5 min to a rapidly stirred solution of *p*-toluenesulfonyl fluoride **1a** (0.10 g, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C. The solution was stirred at -78 °C for 20 min and then alkylated with a solution of MeI (0.20 mL, 2.87 mmol) and HMPA (0.20 mL, 1.15 mmol) in anhydrous THF and stirred for 30 min. The normal workup was followed giving sulfone **5** (0.109 g, 84%) as a pale yellow oil: IR ($CHCl_3$, lit.[25]) 1289, 1136 cm^{-1}.

Preparation of 2-(2-Methylpentyl) *p*-Sulfone (6) via Treatment of *p*-Toluenesulfonyl Fluoride (1a) with *n*-BuLi (3 equiv) Followed by Methyl Iodide. *n*-Butyllithium (0.80 mL, 1.72 mmol) was added dropwise over 5 min to a rapidly stirred solution of *p*-toluenesulfonyl fluoride **1a** (0.10 g, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C. The solution was stirred at -78 °C for 20 min and then alkylated with a solution of MeI (0.20 mL, 2.87 mmol) and HMPA (0.20 mL, 1.15 mmol) in anhydrous THF and stirred for 30 min. The normal workup was followed giving sulfone **6** (0.115 g, 89%) as a pale yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.81 (d, 2 H, J = 8.2 Hz), 7.41 (d, 2 H, J = 8.2 Hz), 2.51 (s, 3 H), 1.70-1.68 (m, 2 H), 1.37-1.02 (m, 2 H), 1.34 (s, 6 H), 0.98 (t, 3 H, J = 7.3 Hz).

[(*p*-Tolylsulfonyl)methylene]cyclohexane (7) via Treatment of *p*-Toluenesulfonyl Fluoride (1a) and (Trimethylsilyl)methyllithium Followed by Cyclohexanone. (Trimethylsilyl)methyllithium (1.6 mL, 1.14 mmol) was added dropwise over 5 min to a rapidly stirred solution of *p*-toluenesulfonyl fluoride (**1a**) (0.1 g, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C and stirred for 2 h. Distilled cyclohexanone (0.06 mL, 0.63 mmol) was added dropwise over 5 min at -78 °C, and the reaction was allowed to warm to rt over 2 h. The normal workup was followed giving sulfone **7** (0.0844 g, 54%) as an oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.74 (d, 2 H, J = 8.0 Hz), 7.28 (d, 2 H, J = 8.0 Hz), 6.11 (s, 1 H), 2.71 (br s, 2 H), 2.39 (s, 3 H), 2.10 (br s, 2 H), 1.53 (br s, 6 H).

Registry No. **2a**, 15310-28-8; **2b**, 94265-66-4; **2k**, 72834-71-0; **3a**, 3185-99-7; **3b**, 7569-36-0; **3c**, 136828-00-7; **3d**, 91968-80-8; **3e**, 5324-90-3; **3f**, 640-57-3; **3g**, 127-63-9; **3h**, 42756-18-3; **3i**, 13894-21-8; **3j**, 67963-06-8; **3k**, 91358-89-3; **3l**, 3112-87-6; **3m**, 5535-52-4; **5**, 29182-78-3; **6**, 136828-01-8; **7**, 136828-02-9; 1 (Ar = *p*-Tol), 455-16-3; 1 (Ar = Ph), 368-43-4; MeLi, 917-54-4; *n*-BuLi, 109-72-8; $TMSCH_2Li$, 1822-00-0; *s*-BuLi, 598-30-1; *t*-BuLi, 594-19-4; PhLi, 591-51-5; Ph_3CLi, 733-90-4; TMSC≡CLi, 54655-07-1; MeMgCl, 676-58-4; *n*-BuMgCl, 693-04-9; PhMgBr, 100-58-3; HC≡CMgBr, 4301-14-8; cyclo-$C_6H_{11}MgCl$, 931-51-1; *i*-BuMgCl, 5674-02-2; allylMgCl, 2622-05-1; vinylMgBr, 1826-67-1; Me_2CuLi, 15681-48-8; *n*-Bu_2CuLi, 24406-16-4; $(TMSCH_2)_2CuLi$, 40988-97-4; *s*-Bu_2CuLi, 23402-73-5; *t*-Bu_2CuLi, 23402-75-7; Ph_2CuLi, 23402-69-9; *n*-BuCuSPhLi, 53128-68-0; $Me_2CuMgCl$, 67234-12-2; *n*-$Bu_2CuMgCl$, 60101-92-0; $Ph_2CuMgBr$, 58938-91-3; $(cyclo\text{-}C_6H_{11})_2CuMgCl$, 62280-27-7; *i*-$Bu_2CuMgCl$, 136828-04-1; $(allyl)_2CuMgCl$, 91550-88-8; *n*-BuPhSCuMgCl, 90384-66-0; MeCu, 1184-53-8; *n*-BuCu, 34948-25-9; *s*-BuCu, 89828-30-8; *t*-BuCu, 56583-96-1; PhCu, 3220-49-3; allylCu, 37974-18-8; *n*-BuCuP(*n*-Bu)$_3$, 26679-41-4; copper(I) iodide, 7681-65-4; cyclohexanone, 108-94-1.

Supplementary Material Available: Elemental analysis results and spectral data on compounds **2a,b**, **2k**, **3a-g**, **3i,j**, **3l**, and **5-7** (3 pages). Ordering information is given on any current masthead page.

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Branched Triangulanes: General Strategy of Synthesis

Nikolai S. Zefirov,*[,†] Sergei I. Kozhushkov,[†] Bogdan I. Ugrak,[†] Kirill A. Lukin,[†] Olga V. Kokoreva,[†] Dmitry S. Yufit,[‡] Yury T. Struchkov,[‡] Stephan Zoellner,[∥] Roland Boese,[§] and Armin de Meijere*[,∥]

Department of Chemistry, Moscow State University, 119899, Moscow, USSR, Nesmeyanov Institute of Organoelement Compounds, 117813, Moscow, USSR, Institut für Anorganische Chemie der Universität-GH Essen, D-4300 Essen, Germany, and Institut für Organische Chemie, Georg-August-Universität Göttingen, D-3400 Göttingen, Germany

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A general synthetic strategy for the construction of *branched triangulanes* (BTs) (spirocondensed polycyclopropanes) has been elaborated. The synthetic utility of the method is illustrated by the synthesis of some members of the [5]- and [6]BT families, especially **13a,b** and **14**. An independent synthesis of the perspirocyclopropanated spiropentane **14** is also presented.

The so-called *triangulanes*, hydrocarbons consisting exclusively of spiro-attached three-membered rings,[1] have interesting stereochemical implications, as elaborated for their simplest subclass, that of *unbranched* triangulanes (UTs) **1**.[1-3] UTs can be prepared by the addition of chloromethylcarbene to methylenecyclopropanes,[2,4-6] subsequent dehydrochlorination with potassium *tert*-butoxide in DMSO,[2,4,6-8] and final cyclopropanation of the

* Authors to whom correspondence should be addressed at Moscow State University or Georg-August-Universität Göttingen.
† Moscow State University.
‡ Nesmeyanow Institute.
§ Universität-GH Essen.
∥ Georg-August-Universität Göttingen.

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