JOC*Article*

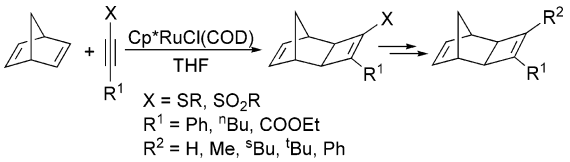
Ruthenium-Catalyzed [2+2] Cycloadditions of Alkynyl Sulfides and Alkynyl Sulfones

Nicole Riddell and William Tam*

Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

wtam@uoguelph.ca

Received November 4, 2005



Ruthenium-catalyzed [2+2] cycloadditions of bicyclic alkenes with alkynyl sulfides and alkynyl sulfones were investigated. The sulfide and sulfone moieties were found to be compatible with the Ru-catalyzed cycloadditions, giving the corresponding cyclobutene cycloadducts in good yields. The sulfonyl-containing cycloadducts can be transformed into a variety of products that are difficult to obtain via direct cycloaddition.

Introduction

We have studied various types of cycloaddition reactions of bicyclic alkenes and are especially interested in those catalyzed by transition metals.[1,2] Transition-metal-catalyzed cycloadditions have demonstrated their usefulness in the formation of rings and complex molecules.[3] The use of transition-metal catalysts provides new opportunities for highly selective cycloaddition reactions, because complexation of the metal to an unactivated alkene, alkyne, or diene significantly modifies the reactivity of this moiety, opening the way for enhanced reactivity and novel reactions. Recent developments in transition-metal-catalyzed [2+2+1],[4] [4+2],[5] [5+2],[6] [4+4],[7] and [6+2][8] cycloaddition reactions have provided efficient methods for the construction of 5−8-membered rings. We and others have studied various aspects of transition-metal-catalyzed [2+2] cycloadditions of an alkene and an alkyne for the synthesis of cyclobutenes, including development of novel catalysts, study of the intramolecular variant of the reaction, investigation of the chemo- and

(1) For our recent contibutions on non-metal-catalyzed cycloaddition reactions of bicyclic alkenes, see: (a) Yip, C.; Handerson, S.; Jordan, R.; Tam, W. *Org. Lett.* **1999**, *1*, 791. (b) Tranmer, G. K.; Keech, P.; Tam, W. *Chem. Commun.* **2000**, 863. (c) Mayo, P.; Hecnar, T.; Tam, W. *Tetrahedron* **2001**, *57*, 5931. (d) Yip, C.; Handerson, S.; Tranmer, G. K.; Tam, W. *J. Org. Chem.* **2001**, *66*, 276. (e) Tranmer, G. K.; Tam, W. *J. Org. Chem.* **2001**, *66*, 5113. (f) Tranmer, G. K.; Tam, W. *Org. Lett.* **2002**, *4*, 4101.

(2) For our recent contibutions on Ru-catalyzed [2+2] cycloadditions, see: (a) Jordan, R. W.; Tam, W. *Org. Lett.* **2000**, *2*, 3031. (b) Jordan, R. W.; Tam, W. *Org. Lett.* **2001**, *3*, 2367. (c) Jordan, R. W.; Tam, W. *Tetrahedron Lett.* **2002**, *43*, 6051. (d) Villeneuve, K.; Jordan, R. W.; Tam, W. *Synlett* **2003**, 2123. (e) Villeneuve, K.; Tam, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 610. (f) Jordan, R. W.; Khoury, P. K.; Goddard, J. D.; Tam, W. *J. Org. Chem.* **2004**, *69*, 8467. (g) Villeneuve, K.; Riddell, N.; Jordan, R. W.; Tsui, G. C.; Tam, W. *Org. Lett.* **2004**, *6*, 4543. (h) Riddell, N.; Villeneuve, K.; Tam, W. *Org. Lett.* **2005**, *7*, 3681.

(3) For reviews on transition-metal-catalyzed cycloadditions, see: (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (b) Hegedus, L. S. *Coord. Chem. Rev.* **1997**, *161*, 129. (c) Wender, P. A.; Love, J. A. *Advances in Cycloaddition*; JAI Press: Greenwich, 1999; Vol. 5, pp 1−45.

(4) For recent reviews on transition-metal-catalyzed [2+2+1] cycloadditions, see: (a) Pericas, M. A.; Balsells, J.; Castro, J.; Marchueta, I.; Moyano, A.; Riera, A.; Vazquez, J.; Verdaguer, X. *Pure Appl. Chem.* **2002**, *74*, 167. (b) Sugihara, T.; Yamaguchi, M.; Nishizawa, M. *Chem.—Eur. J.* **2001**, *7*, 1589. (c) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263. (d) Buchwald, S. L.; Hicks, F. A. In *Comprehensive Asymmetric Catalysis I-III*; Jabosen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; Vol. 2, pp 491−510. (e) Keun Chung, Y. *Coord. Chem. Rev.* **1999**, *188*, 297.

(5) (a) Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 6432. (b) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965. (c) Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *117*, 1843. (d) O'Mahoney, D. J. R.; Belanger, D. B.; Livinghouse, T. *Synlett* **1998**, 443. (e) Murakami, M.; Ubukata, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2248. (f) Paik, S.-J.; Son, S. U.; Chung, Y. K. *Org. Lett.* **1999**, *1*, 2045. (g) Hilt, G.; Smolko, K. I. *Angew. Chem., Int. Ed.* **2003**, *42*, 2795. (h) Witulski, B.; Lumtscher, J.; Bergsträber, U. *Synlett* **2003**, 708. (i) Hilt, G.; Lüers, S.; Harms, K. *J. Org. Chem.* **2004**, *69*, 624.

(6) (a) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. (b) Wender, P. A.; Rieck, H.; Fuji, M. *J. Am. Chem. Soc.* **1998**, *120*, 10976. (c) Trost, B. M.; Shen, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2313. (d) Wender, P. A.; Williams, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4550.

(7) (a) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. (b) Wender, P. A.; Nuss, J. M.; Smith, D. B.; Suarez-Sobrino, A.; Vagberg, J.; Decosta, D.; Bordner, J. *J. Org. Chem.* **1997**, *62*, 4908.

(8) Wender, P. A.; Correa, A. G.; Sato, Y.; Sun, R. *J. Am. Chem. Soc.* **2000**, *122*, 7815.

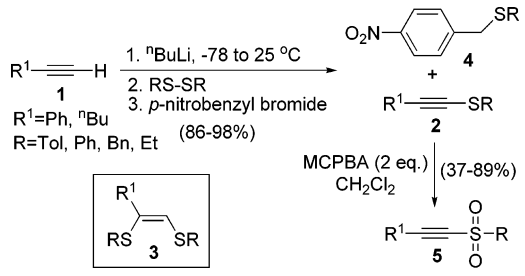
10.1021/jo052295a CCC: $33.50
Published on Web 02/03/2006

regioselectivity of unsymmetrical substrates, and asymmetric induction studies using chiral auxiliaries on the alkyne component.[2,9−11] However, most of the alkynes employed thus far in transition-metal-catalyzed [2+2] cycloadditions have only contained carbon substituents such as alkyl, aryl, ester, and ketone functionalities. There are only two examples of the use of heteroatom-substituted acetylenic substrates (alkynyl halides and ynamides)[2g,2h] in ruthenium-catalyzed [2+2] cycloadditions reported in the literature. In this paper, we report the first examples of ruthenium-catalyzed [2+2] cycloadditions of bicyclic alkenes with alkynyl sulfides and alkynyl sulfones. This investigation provides valuable information on the compatibility and reactivity of sulfur-containing alkynes in ruthenium-catalyzed [2+2] cycloadditions. The sulfide/sulfone moiety can also be used for further functionalization, thereby providing a complementary method for the preparation of those cycloadducts that are difficult to obtain via direct cycloaddition. Finally, because sulfur-containing compounds with therapeutic properties are widespread,[12] the incorporation of sulfur into the cycloadduct could be beneficial.

Results and Discussion

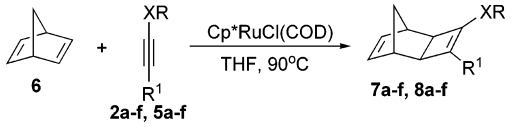
To begin this study, several alkynyl sulfides and alkynyl sulfones were prepared (Scheme 1). There are several procedures

SCHEME 1. Synthesis of Alkynyl Sulfides 2 and Alkynyl Sulfones 5



available for the preparation of alkynyl sulfides,[13] but we found that the simplest and most generally applicable method was developed by MaGee and Kabanyane.[13b] The procedure involves the treatment of a terminal alkyne with *n*-BuLi and the trapping of the resulting acetylide anion with various disulfides to provide alkynyl sulfides **2**. Because the thiolate anion (RS^-) generated in the second step of this reaction is prone to undergo addition to the resulting alkynyl sulfide **2**, a bis-sulfide side product **3** is formed in the reaction leading to lowered yields of the desired alkynyl sulfides. To overcome this problem, MaGee and Kabanyane used methyl iodide as an efficient thiolate trap to remove the thiolate anion from the reaction mixture. However, we found that purification of the alkynyl sulfides **2** proved to be difficult by flash chromatography, because the methyl phenyl sulfide formed using the methyl iodide trap had a very similar R_f value to that of the desired alkynyl sulfide **2**. Thus, we modified the reaction by trapping the thiolate anion with *p*-nitrobenzyl bromide instead of methyl iodide. The resulting sulfide **4** was much more polar than the desired alkynyl sulfide **2**, and they could be separated easily by flash chromatography. Alkynyl sulfones **5** were prepared by the oxidation of alkynyl sulfides **2** using MCPBA (2 equiv) in dichloromethane.[13,14]

TABLE 1. Ru-Catalyzed [2+2] Cycloaddition of Norbornadiene 6 with Alkynyl Sulfides 2a−f and Alkynyl Sulfones 5a−f



entry	alkyne[a]	XR	R^1	cycloadduct	yield[b] (%)
1	**2a**	SEt	Ph	**7a**	76
2	**2b**	SBn	Ph	**7b**	80 (12)
3	**2c**	SPh	Ph	**7c**	78
4	**2d**	STol	Ph	**7d**	78
5	**2e**	STol	*n*-Bu	**7e**	23 (55)
6	**2f**	STol	COOEt	**7f**	78
7	**5a**	SO_2Et	Ph	**8a**	55
8	**5b**	SO_2Bn	Ph	**8b**	66
9	**5c**	SO_2Ph	Ph	**8c**	84
10	**5d**	SO_2Tol	Ph	**8d**	84
11	**5e**	SO_2Tol	*n*-Bu	**8e**	64
12	**5f**	SO_2Tol	COOEt	**8f**	0[c]

[a] For alkynyl sulfides **2a−f**, the reactions were stirred for 168 h. For alkynyl sulfones **5a−f**, the reactions were stirred for 72 h. [b] The yield of the isolated cycloadducts after column chromatography. The yield of the recovered alkyne is shown in brackets. [c] Decomposition of the alkynyl sulfone **5f** was observed.

Both the alkynyl sulfide and the alkynyl sulfone moieties were found to be compatible with the ruthenium-catalyzed [2+2] cycloadditions. In the presence of 5−10 mol % of the catalyst, Cp*RuCl(COD) (COD = 1,5-cyclooctadiene, Cp* = 1,2,3,4,5-pentamethylcyclopentadiene), [2+2] cycloadditions of norbornadiene **6** with alkynyl sulfides **2a−f** and alkynyl sulfones **5a−f** occurred smoothly at 90 °C to provide the corresponding cycloadducts in moderate to good yields (Table 1). In all cases, only the exo cycloadducts were formed.[15] Very little reaction was observed when the cycloadditions were carried at a lower temperature. Alkynyl sulfides **2** were found to be less reactive than the corresponding alkynyl sulfones **5** and required a longer reaction time to reach completion. In the cases of alkynyl sulfides **2** (entries 1−6), when R^1 = Ph (entries 1−4), the change of the substituent (R) on the sulfur had little effect on the yields of the cycloadditions. However, when R^1 = an alkyl group (entry 5), the cycloaddition was much slower, and even after prolonged heating (90 °C for 168 h), only 23% of the

(9) Trost, B. M.; Yanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294.

(10) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

(11) (a) Huang, D.-J.; Rayabarapu, D. K.; Li, L.-P.; Sambaiah, T.; Cheng, C.-H. *Chem.—Eur. J.* **2000**, *6*, 3706. (b) Chao, K. C.; Rayabarapu, D. K.; Wang, C.-C.; Cheng, C.-H. *J. Org. Chem.* **2001**, *66*, 8804.

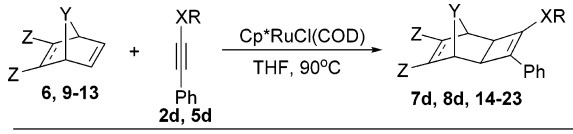
(12) (a) Block, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135. (b) Sutton, A. E.; Clardy, J. *J. Am. Chem. Soc.* **2001**, *123*, 9935. (c) Kouokam, J. C.; Zapp, J.; Becker, H. *Phytochemistry* **2002**, *60*, 403. (d) Iranshahi, M.; Amin, G.-R.; Amini, M.; Shafiee, A. *Phytochemistry* **2003**, *63*, 965.

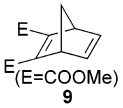
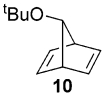
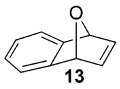
(13) (a) Miyachi, N.; Shibasaki, M. *J. Org. Chem.* **1990**, *55*, 1975. (b) Kabanyane, S. T.; MaGee, D. I. *Can. J. Chem.* **1992**, *70*, 2758. (c) Braga, A. L.; Reckziegel, A.; Menezes, P. H.; Stefani, H. A. *Tetrahedron Lett.* **1993**, *34*, 393. (d) Takeda, H.; Shimada, S.; Ohnishi, S.; Nakanishi, F.; Matsuda, H. *Tetrahedron Lett.* **1998**, *39*, 3701. (e) Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2001**, *3*, 91. (f) Back, T. G. *Tetrahedron* **2001**, *57*, 5263.

(14) For the oxidation of sulfides to sulfones, see: (a) Sandrinelli, F.; Perrio, S.; Beslin, P. *Org. Lett.* **1999**, *1*, 1177. (b) Shukla, V. G.; Salgaonkar, P. D.; Akamanchi, K. G. *J. Org. Chem.* **2003**, *68*, 5422. (c) Iranpoor, N.; Firouzabadi, H.; Pourali, A.-R. *Synlett* **2004**, 347.

(15) For the determination of the exo and endo stereochemistry of [2+2] cycloadducts, see our previous work in ref 2. Also, no cycloaddition with the COD ligand was observed, as this type of Ru-catalyzed [2+2] cycloaddition was known to occur only on strained bicyclic alkenes; see refs 2 and 10.

TABLE 2. Ru-Catalyzed [2+2] Cycloaddition of Different Bicyclic Alkenes with Alkynyl Sulfide 2d and Alkynyl Sulfone 5d



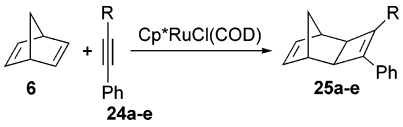
entry	alkene	alkyne[a]	XR	cycloadduct	yield (%)[b]
1		**2d**	STol	**7d**	78
2		**5d**	SO_2Tol	**8d**	84
3		**2d**	STol	**14**	84
4		**5d**	SO_2Tol	**15**	83
5		**2d**	STol	**16**	0[c]
6		**5d**	SO_2Tol	**17**	32
7		**2d**	STol	**18**	0[c]
8		**5d**	SO_2Tol	**19**	68
9		**2d**	STol	**20**	35[d]
10		**5d**	SO_2Tol	**21**	89
11		**2d**	STol	**22**	78
12		**5d**	SO_2Tol	**23**	53

[a] For alkynyl sulfide **2d**, the reactions were stirred for 168 h. For alkynyl sulfone **5d**, the reactions were stirred for 72 h. [b] The yield of the isolated cycloadducts after column chromatography. [c] Only the starting materials were recovered. [d] Alkynyl sulfide **2d** was recovered in the amount of 34%.

cycloadduct **7e** was produced and 55% of the starting alkynyl sulfide **2f** was recovered. A simliar trend was observed with alkynyl sulfones **5a**−**e**. It is worth noting that alkynyl sulfide **2f** (with R^1 = COOEt, entry 6) undergoes cycloaddition with norbornadiene to provide cycloadduct **7f** in good yield, but the corresponding alkynyl sulfone **5f** (with R^1 = COOEt, entry 12) failed to produce any cycloadduct, and only decomposition of the sulfone starting material was observed.

To determine the general applicability of alkynyl sulfides and alkynyl sulfones in the ruthenium-catalyzed [2+2] cycloaddition, a few different bicyclic alkenes were chosen for further investigation, and the results are shown in Table 2. The Ru-catalyzed [2+2] cycloadditions of 2,3-disubstituted norbornadiene **9** with both alkynyl sulfide **2d** and alkynyl sulfone **5d** were highly chemo- and stereoselective (entries 3 and 4), giving single chemo- and stereoisomers in good yields. In both cases, the cycloaddition only occurred on the less-substituted double bond of the substituted norbornadienes, and only exo cycloadducts were formed. No other isomeric cycloadducts were detected by a 400-MHz ^{1}H NMR in the crude reaction mixtures. We have previously shown that 7-*tert*-butoxynorbornadiene **10** is much less reactive than the parent norbornadiene **6**;[2f] in fact, only the more reactive alkynyl sulfone **5d** undergoes cycloaddition with 7-*tert*-butoxynorbornadiene **10**, giving the [2+2] cycloadduct **17** in low yield (32%), and the less reactive alkynyl sulfide **2d** was completely unreactive (entries 5 and 6). A similar trend was observed with 7-phenylnorbornadiene **11** (entries 7 and 8). Both the cycloadditions of 7-substituted norbornadienes **10** and **11** with alkynyl sulfone **5d** were highly chemo- and stereoselective (entries 6 and 8), giving only the anti,exo cycloadducts in moderate yields. Ru-catalyzed [2+2] cycloadditions of norbornene **12** and 7-oxabicyclic alkene **13** with both alkynyl sulfide **2d** and alkynyl sulfone **5d** also produced the corresponding [2+2] cycloadducts in moderate to good yields (entries 9−12).

TABLE 3. Ru-Catalyzed [2+2] Cycloaddition of Norbornadiene 6 and Unactivated Alkynes

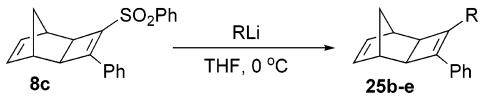


entry	alkyne	R	temperature (°C)	time (h)	yield[a] (%)
1	**24a**	H	80	16	44[b]
2	**24b**	Me	95	90	22[c]
3	**24c**	*s*-Bu	95	168	0[c]
4	**24d**	*t*-Bu	95	168	0[c]
5	**24e**	Ph	80	16	23[c]

[a] The yield of the isolated cycloadducts **25**. [b] Homotrimerization of the terminal alkyne **24a** was observed, see ref 10. [c] The starting alkyne was recovered in the amount of 55−85%.

To illustrate the synthetic usefulness of the resulting sulfonyl containing cycloadducts, cycloadduct **8c** was converted to various products (**25a**−**e**, Table 4 and Scheme 2) that are difficult to obtain via direct cycloaddition. Although the Ru-catalyzed [2+2] cycloaddition of bicyclic alkenes with electron-deficient alkynes usually produced cyclobutene cycloadducts in good yields,[2] alkynes that do not contain an electron-withdrawing group have proven to be poor reaction partners in the Ru-catalyzed [2+2] cycloadditions (Table 3).[2g] For example, the Ru-catalyzed [2+2] cycloaddition of norbornadiene **6** and terminal alkyne **24a** gave the corresponding cyclobutene cycloadduct in only 44% yield, and homotrimerization of the terminal alkyne **24a** was observed (entry 1). Alkynes **24b** (R = Me) and **24e** (R = Ph) were also found to be less unreactive, giving the cycloadducts **25b** and **25e** in low yields (entries 2 and 5) even after prolonged heating at elevated temperatures. The more sterically bulky alkynes **24c** and **24d** were completely unreactive (entries 3 and 4) in the Ru-catalyzed [2+2] cycloadditions. Thus, these cycloadducts **25a**−**e** are difficult to obtain via a direct [2+2] cycloaddition.

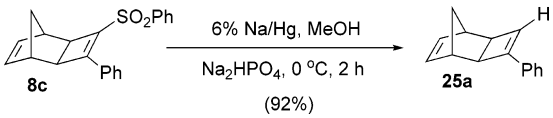
TABLE 4. Reaction of the Sulfonyl-Containing Cycloadduct 8c with Various Organolithium Reagents



entry	R	product	yield[a] (%)
1	Me	**25b**	80
2	*s*-Bu	**25c**	76
3	*t*-Bu	**25d**	46
4	Ph	**25e**	95

[a] The yield of the isolated cycloadducts after column chromatography.

SCHEME 2. Desulfonation of Cycloadduct 5c



Knochel and co-workers have recently shown that vinyl sulfones in strained ring systems can undergo a reaction with organolithium reagents, and the sulfone moiety can be replaced by various alkyl and aryl groups.[16] To our delight, when our sulfonyl-containing cycloadduct **8c** was treated with various organolithium reagents, products **25b**−**e** were obtained in moderate to excellent yields (Table 4). An increase in the size of the alkyl group of the organolithium reagent from primary (R = Me) to secondary (R = *s*-Bu) to tertiary (R = *t*-Bu) led to a decrease in the yield of the reactions (entries 1−3). The addition of PhLi to **8c** gave cycloadduct **25e** in excellent yield (entry 4). Desulfonation of the sulfonyl-containing cycloadduct **8c** was also achieved using a 6% Na/Hg sodium amalgam, which resulted in the formation of **25a** in excellent yield (Scheme 2).[17]

Conclusion

In summary, we have demonstrated the first examples of Ru-catalyzed [2+2] cycloadditions of bicyclic alkenes with alkynyl sulfides and alkynyl sulfones. We found the alkynyl sulfide and alkynyl sulfone moieties to be compatible with the Ru-catalyzed [2+2] cycloadditions, and the reactivity of the alkynyl sulfones was generally greater than that of the alkynyl sulfides. The Ru-catalyzed [2+2] cycloadditions of alkynyl sulfides and alkynyl sulfones with various bicyclic alkenes were also highly chemo- and stereoselective, giving the cyclobutene cycloadducts as single chemo- and stereoisomers in moderate to good yields. Finally, it was found that the sulfonyl-containing cycloadducts could be converted to cycloadducts that are difficult to obtain via direct cycloaddition. Further investigations on the use of other sulfur-containing alkynes (e.g., chiral alkynyl sulfoxides and chiral sulfinate esters) in Ru-catalyzed [2+2] cycloadditions, and the use of the cycloadducts for the synthesis of more complex polycyclic natural products are currently in progress in our laboratory.

Experimental Section[18]

Only a representative procedure of the ruthenium-catalyzed [2+2] cycloaddition and characterization of a cycloadduct is described here. For the synthesis of alkynyl sulfides and alkynyl sulfones and full details of other ruthenium-catalyzed [2+2] cycloadditions, see Supporting Information.

General Procedure for Ruthenium-Catalyzed [2+2] Cycloadditions. A mixture of bicyclic alkene (2.5−5 equiv),[19] alkynyl sulfur substrate (1 equiv), and THF was prepared in an oven-dried vial. The contents of this vial were then transferred via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out in a drybox, 5−10 mol %) under nitrogen. The reaction mixture was stirred in the dark at 90 °C for 72−168 h. The crude product was purified by flash chromatography to give the corresponding cycloadduct (hexanes or ethyl acetate/hexanes mixture).

Cycloadduct 7a (Table 1, Entry 1). Following the above general procedure with norbornadiene **6** (65.0 μL, 0.603 mmol), alkynyl sulfide **2a** (29.9 mg, 0.184 mmol), THF (0.3 mL), and Cp*RuCl(COD) (7.4 mg, 0.020 mmol), the reaction mixture was stirred in the dark at 90 °C for 168 h. The crude product was purified by column chromatography (hexanes) to provide cycloadduct **7a** (35.5 mg, 0.140 mmol, 76%) as a colorless oil: R_f 0.54 (EtOAc/hexanes = 1:9); IR (CH_2Cl_2, NaCl) 3056 (m), 3024 (w), 2969 (s), 2928 (s), 2871 (w), 1603 (s), 1488 (s), 1446 (s), 1263 (s), 1191 (s), 775 (s), 762 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.43−7.46 (m, 2H), 7.29−7.38 (m, 2H), 7.20 (m, 1H), 6.24 (dd, 1H, J = 3.1, 5.5 Hz), 6.18 (dd, 1H, J = 3.1, 5.5 Hz), 2.82−3.00 (m, 2H), 2.73 (s, 1H), 2.73 (d, 1H, J = 2.4 Hz), 2.69 (m, 1H), 2.63 (br s, 1H), 1.48 (m, 2H), 1.38 (t, 3H, J = 7.4 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 139.7, 136.6, 135.3, 135.1, 134.1, 128.3, 126.5, 125.7, 46.1, 43.3, 40.4, 39.8, 39.7, 25.6, 16.1. HRMS (*m*/*z*): calcd for $C_{17}H_{18}S$, 254.1129; found, 254.1134. Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13. Found: C, 80.10; H, 7.46.

Acknowledgment. This work was supported by NSERC (Canada) and Boehringer Ingelheim (Canada) Ltd. W.T. thanks Boehringer Ingelheim (Canada) Ltd. for a Young Investigator Award. N.R. thanks the Ontario Government for a postgraduate scholarship (OGSST). Professor Adrian Schwan in our department is thanked for helpful discussions.

Supporting Information Available: Detailed experimental procedures and compound characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO052295A

(16) Knapp, K. M.; Goldfuss, B.; Knochel, P. *Chem.—Eur. J.* **2003**, *9*, 5259.

(17) For examples involving the use of a Na/Hg sodium amalgam to remove vinyl sulfones, see: (a) Kato, M.; Watanabe, M.; Awen, B. Z. *J. Org. Chem.* **1993**, *58*, 5145. (b) Clayden, J.; Kenworthy, M. N.; Helliwell, M. *Org. Lett.* **2003**, *5*, 831.

(18) General methods were described in previous publications; see refs 1(d) and 2(f).

(19) As we previously reported and explained in refs 2a and 2e, decreasing the number of equivalents of the alkene component greatly reduced the yield of the [2+2] cycloadditions.