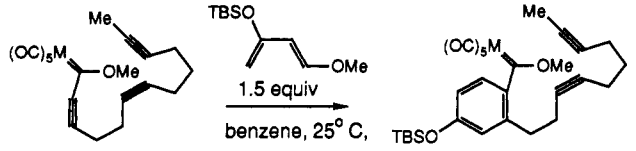
rapidly decomposing intermediate complex could be observed by TLC, which was presumably the nonaromatized Diels-Alder adduct; however, these complexes did not survive when **11** and **12** were purified on silica gel.

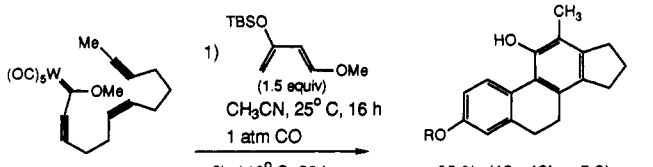


3 ~0.1 M

11 M = Cr 87%
12 M = W 82%

Although the thermolysis of **11** at 75 °C did produce a better mass balance than did **6c**, the reaction still gives an equal distribution between phenol and lactone products, as indicated in Scheme II. According to the mechanism shown in Scheme II, the branch point between the lactone and phenol products is the vinyl carbene intermediate **13**, which undergoes either insertion of the second equivalent of alkyne to give **14** or CO insertion to give the ketene complex **15**. If this is correct, then a solution to the poor chemoselectivity would be to employ tungsten carbene complexes since it has been observed that tungsten carbene complexes give CO-inserted products less readily than chromium.[12] In fact, the thermolysis of the tungsten complex **12** at 110 °C gives exclusively the two-alkyne phenol **18** in 78% yield in acetonitrile solution under CO atmosphere. Likewise, lactone products were never observed from the thermolysis of the tungsten complexes **7a-c** indicated in Table I.

Finally, it was found that all four rings of the tetracyclic phenol **18** could be constructed in one pot in 62% yield from the triyne carbene complex **3b**.[13] This carbene complex could be readily obtained in two steps from the triflate **5** and the commercially available 1,5-hexadiyne as indicated in Scheme I.[15] This strategy for the synthesis of steroids is in the class 0 → ABCD and has been reported previously in a cobalt-mediated process.[17] The results described herein reveal that the two-alkyne annulations and Diels-Alder reactions of Fischer carbene complexes applied in tandem provide for a very straightforward approach to the steroid ring system. The strategy would be amenable to nonaromatic A-ring systems upon generation of **2** from the Diels-Alder reactions of α,β-vinylic carbene complexes.



3b 0.05 M

62% (**18a**:**18b** = 5.2)
18a R = TBS, **18b** R = H

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Supplementary Material Available: Spectral data for all new compounds (6 pages). Ordering information is given on any current masthead page.

(11) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7656. (c) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23.

(12) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

(13) Upon completion of the Diels-Alder reaction (16 h), the solution was diluted 10-fold with acetonitrile, then sealed in a reaction flask with a threaded stopcock[14] at 25 °C under 1 atm of CO, and heated to 110 °C for 23 h.

(14) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

(15) 1,5-Hexadiyne was deprotonated with 1.0 equiv of *n*-butyllithium in THF at -78 °C, then treated with 1.0 equiv of triflate **5**,[6d] and upon warming to 0 °C gave a 55% yield of triyne **4a**. The triyne **4a** was converted to complexes **3a** and **3b** in 66 and 52% yields, respectively, according to procedures for related alkynyl carbene complexes.[16]

(16) Chan, K. S.; Wulff, W. D. *J. Org. Chem.* **1986**, *108*, 5239.

(17) Lecker, S. H.; Nguyen, N. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 856.

Free Radical Ring Expansion of Fused Cyclobutanones: A New Ring Expansion Annulation Stratagem

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The Diels-Alder reaction is highly valued because it can be employed to append four carbons stereospecifically to an alkene to form a new six-membered ring. Similar stereospecific annulation strategies have been developed for fusing one, two, and three carbons to alkenes to synthesize three-, four-, and five-membered rings. So too, it would be useful to append five, six, or more carbons to appropriate alkenes to form seven-, eight-, or higher-membered rings in stereospecific fashion. We have discovered a new synthetic method which accomplishes this goal.

The procedure is straightforward. An ω-bromoalkyl ketene is generated from an appropriate ω-bromo acid in the presence of an alkene to form a cyclobutanone[1,2] (Scheme I). Free radical reaction[3] of the adduct yields the ring-expanded[4] annulation product (Scheme I).

The reaction sequence leading to the ring fusion is stereospecific; the cis stereochemistry is enforced by the requirements of the cyclobutanone ring and is then translated to the ring-expansion product. Further examples are shown in Table I.

In the ketene cycloaddition, a mixture of exo and endo products is observed. The cycloadducts with exo side chains undergo smooth ring expansion. Cyclobutanones with endo side chains are prone to undergo direct reduction as a consequence of steric hindrance to ring-closure.

In a typical example (Table I, entry 1) the exo adduct **1** of cyclopentadiene and bromopropyl ketene was treated under slow addition conditions with tri-*n*-butyltin hydride and AIBN in refluxing benzene. The product of ring annulation **2** was obtained in 74% yield together with minor amounts of the alternative ring-opening product **3** and the product **4** of cyclization to the double bond.

In designing this sequence, we anticipated that the initial primary radical in **5** would attack the four-membered ketone to give the alkoxy radical[4,5] (Scheme II). The latter would then open in either of two ways (to **7** or **8**) to yield the ring-expanded annulation product **2** accompanied by the minor product of ring attachment **3**. The driving force is provided by the relief of strain in the four-membered ring. In every instance, ring expansion is the major path in the sequence.

Entry 2 in Table I shows that annulation of eight-membered rings is also possible following this strategy. Annulation to cy-

(1) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. Ghosez, L.; O'Donnell, M. J. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. II, pp 79-140.

(2) Regio- and stereoselectivity of ketene-olefin cycloadditions: Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754. Valenti, E.; Pericas, M. A.; Moyano, A. *J. Org. Chem.* **1990**, *55*, 3582. Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106.

(3) For recent reviews of free radical reactions, see: Curran, D. P. *Synthesis* **1988**, *417*, 489. Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541.

(4) For free radical ring-expansions, see: Dowd, P.; Choi, S.-C. *Tetrahedron* **1991**, *47*, 4847 and references therein.

(5) Intramolecular addition of alkyl radicals to carbonyl groups: Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1991**, *113*, 5791. Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674. Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 230.

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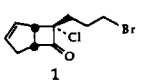
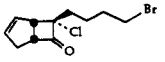
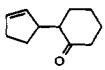
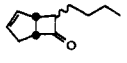
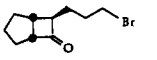
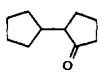
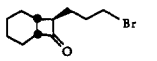
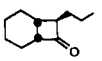
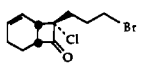
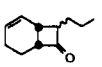
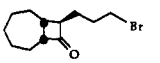
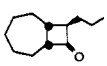
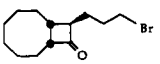
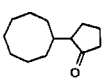
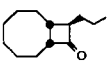
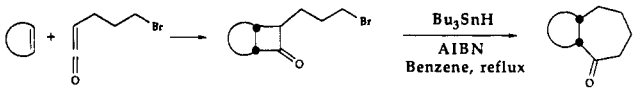
Table I. Free Radical Ring Expansion Reactions

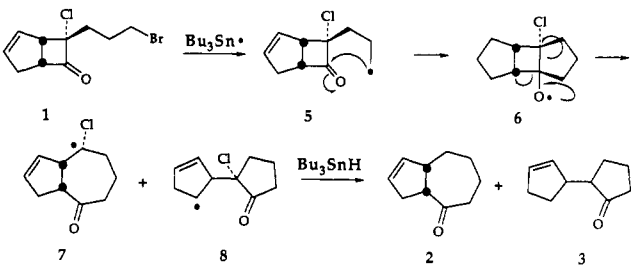
entry	substrate	conditions [a]	products and relative yields [b]		
1	 1	A	 2 74% (80%) [c]	 3 18%	 4 8% (4%)
2		A	 59% (54%)	 28% (19%)	 13% (8%)
3	 9	(a) C	 10 68%	 11 11%	 12 21%
		(b) B	23%	12%	65% (58%)
4		B	 65% (63%)	 16% (16%)	 19% (16%)
5		A	 18 55% (71%) [d]	 19 23%	 14% (13%)
6		B	 67% (64%)	 17% (11%)	 16% (14%)
7		B	 45% (43%)	 32% (30%)	 9% (7%)

[a] (A) 7–10 h slow addition of 2.0–3.3 equiv of Bu_3SnH with AIBN to refluxing benzene. (B) 7 h slow addition of 1.5 equiv of Bn_3SnH with AIBN to refluxing benzene. (C) 1.5 equiv of Bu_3SnH (7.5 mM), AIBN, benzene, reflux. [b] Relative yields refer to normalization on GC-MS. Figures in parentheses are isolated yields after flash column chromatography. [c] Mixture of **2** and **3**. [d] Mixture of **18** and **19**.

Scheme I



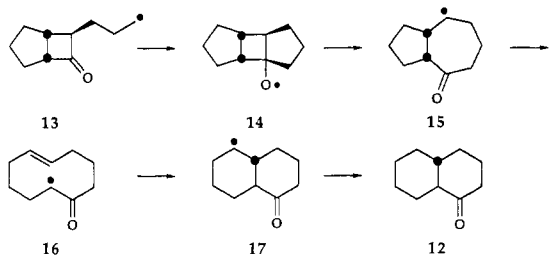
Scheme II



cloheptene (entry 6) and to cyclooctene (entry 7) offers attractive extensions of the method.

In the example shown in entry 3 the outcome depends critically on the reaction conditions. Thus, if the bromide **9** is heated with a relatively high concentration of tri-*n*-butyltin hydride (entry 3a), ring annulation yielding **10** is the major course (68%) of the reaction. Also produced are the product of ring attachment **11** (11%) and the product of rearrangement, *trans*-α-decalone (**12**, 21%). If the reaction is carried out under conditions of slow addition of tri-*n*-butyltin hydride (entry 3b), *trans*-α-decalone (**12**) becomes the major product (65%). We suggest that the reaction leading to *trans*-α-decalone proceeds through a series of radical intermediates as shown in Scheme III. Thus, the initial primary radical **13** adds to the cyclobutanone carbonyl group yielding the reactive alkoxy radical **14**. Ring opening leads to the fused bicyclo[5.3.0]decanone radical **15** which can then revert to the

Scheme III



cyclodecanone acyl-substituted radical **16**.[6,7] Ring closure in the alternative sense to **17** is then followed by hydrogen atom chain transfer yielding *trans*-α-decalone (**12**).

In summary, we have discovered a new means of appending five or six carbons to alkenes, leading to cyclic products carrying useful levels of functionality.

Acknowledgment. This research was generously supported by the Institute for General Medical Sciences of the National Institute of Health under Grant 39825. It is a pleasure to thank Professor Dennis P. Curran for his helpful comments.

Supplementary Material Available: Listing of ketene cycloaddition reactions (1 page). Ordering information is given on any current masthead page.

(6) β-scission of alkoxy radicals: Pattenden, G.; Ellwood, C. W. *Tetrahedron Lett.* **1991**, *32*, 1591. O'Dell, D. E.; Loper, J. T.; MacDonald, T. L. *J. Org. Chem.* **1988**, *53*, 5225. Suginome, H.; Senboku, H.; Yamada, S. *Tetrahedron Lett.* **1988**, *29*, 79. Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718. MacDonald, T. L.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1501.

(7) Curran, D. P.; Morgan, T. M.; Schwartz, C. E.; Snider, B. B.; Dombrowski, M. *J. Am. Chem. Soc.* **1991**, *113*, 6607. Broeker, J. L.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 3651 and references therein.