compounds **2a**, **2c**, and **3**. Peptide ureas **1d** and **1e** also exhibit downfield shifting of only one NH group in the ^1H NMR and show both free and hydrogen-bonded N–H stretches in the IR.

The fraction of intramolecular hydrogen bonding in ureas **1** and **3** was determined by infrared and ^1H NMR spectroscopy. Comparison of the integrated absorbances of the free NH signals of **3** (3459 cm^{-1}) and **2a** (3464 cm^{-1}) indicates that 15 ± 5% of **3** is in a non-hydrogen-bonded conformation. Integration of the shoulder at 3455 cm^{-1} in **1b** (as the difference infrared absorption spectrum of **1b** and **2c**) reveals that 15 ± 5% of **1b** is in a non-hydrogen-bonded conformation. On the basis of these data and the ^1H NMR spectra of **1b**, **3**, and **2c**, we estimate the chemical shift of a fully hydrogen bonded NH group to be 2.5 ppm downfield of the free NH resonance in this family of urea derivatives. The percentages of intramolecular hydrogen bonding in ureas **1a**, **1c–1e** was estimated using this value. Table I summarizes these results.

These findings suggest that oligoureas of the general structure **1** may prove useful as *molecular scaffolding* to orient different groups in a parallel fashion off an oligoamine backbone. We are currently investigating this application and will report further results shortly.

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Supplementary Material Available: Experimental details for the preparation and spectroscopic characterization of all compounds described in the text (ureas 1–3) (17 pages). This material is contained in many 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.

Rearrangements of 4-Alkynylcyclobutenones. Annelated Spiroepoxycyclohexadienones and Quinones from 4-(1,5-Dialkynyl)-4-methoxy(or hydroxy)cyclobutenones

Haiji Xia and Harold W. Moore*

Department of Chemistry, University of California, Irvine, California 92717

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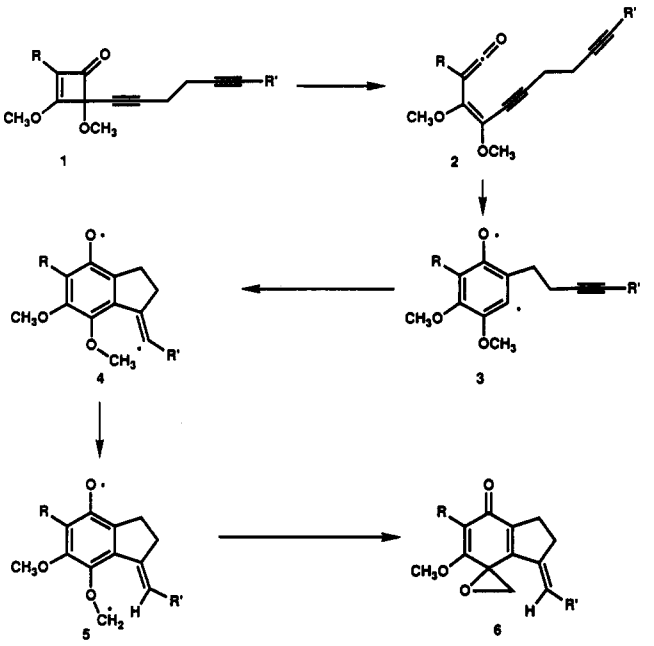
Summary: 4-(1,5-Dialkynyl)-4-methoxycyclobutenones **1** were shown to undergo a unique rearrangement to annelated spiroepoxides **6** upon thermolysis in toluene. The 4-hydroxy analogs also ring expand giving either quinones **13** or **14** as a function of the reaction solution concentration. This concentration dependence provides evidence for further mechanistic details of the general quinone synthesis stemming from 4-alkynyl-4-hydroxycyclobutenones.

Reported here are two unique ring expansions of 4-alkynylcyclobutenones; one leads to spiroepoxycyclohexadienones **6** and the other to annelated quinones **13**. *The spiroepoxides stem from 4-(1,5-dialkynyl)-4-methoxycyclobutenones* ***1a–f*** *which rearrange to* ***6a–f*** *in refluxing toluene (Scheme I).*[1] A reasonable mechanism involves initial formation of the enynylketenes **2** which lead to the diradicals **3**. The more reactive ring-based radical center undergoes exo addition to the proximal alkyne moiety to give **4**, and the resulting vinyl radical then abstracts a H-atom from the adjacent methoxy group to give **5** which leads directly to the spiroepoxides **6**.[2–4]

Scheme I



	R	R'	Yield
a)	OCH_3	H	54%
b)	OCH_3	C_6H_5	87%
c)	OCH_3	$C(CH_3)_2OBn$	62%
d)	C_6H_5	C_6H_5	71%
e)	OCH_3	C_6H_5	91%
f)	OCH_3	$(CH_2)_3CH{=}CH_2$	70%

The above annelation sequence is dependent upon the distance between the two alkynyl groups in the 4-substituent of the starting 4-methoxycyclobutenones. For example, the diradicals generated from **7a,b**, unlike those

(1) In a previous contribution the rearrangement of 4-alkynyl-4-(propargyloxy)cyclobutenones to methylenebenzofurans was described. See: Xu, S.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 6104.

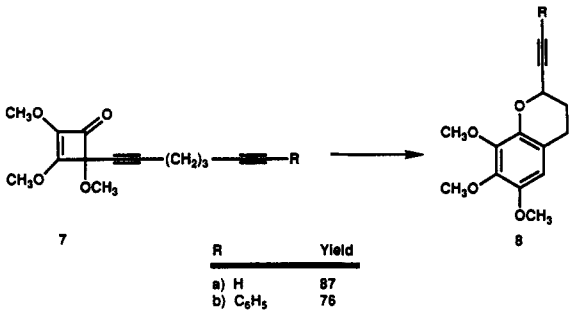
(2) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(3) For excellent reviews on radical cyclizations see: (a) Jasperse, C.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237. (b) Curran, D. P. *Synthesis* **1988**, *6*, 417–39. (c) Curran, D. P. *Synthesis* **1988**, *7*, 489–513. (d) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: New York, 1986.

(4) Structure assignments are based on characteristic spectral properties. The *E*-stereochemistry of the alkylidene group in **6a–f** is based upon difference NOE studies. For **13c** a single-crystal X-ray structure was obtained.

0022-3263/92/1957-3765$03.00/0

Scheme II



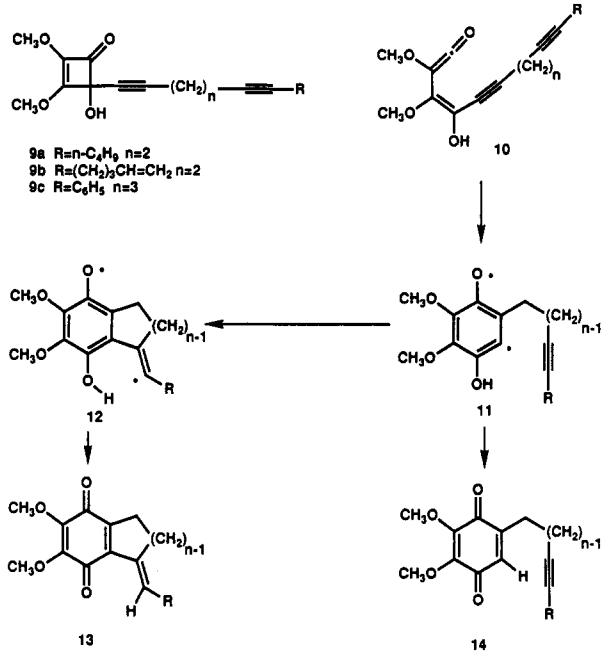
from **1a–f**, sustain a 1,5-H transfer to give the corresponding propargyl radicals and these then ring close to the chromanols **8a,b** in, respectively, 87% and 76% isolated yield.

Thermolyses of the 4-alkynyl-4-hydroxycyclobutenones **9a–c** were also found to undergo ring expansions, but quinones rather than spiroepoxides were realized. Surprisingly, the course of the reactions was observed to be concentration dependent. For example, thermolyses (110 °C, 2 h) of a toluene solution of **9a** at high dilution (3.86×10^{-3} M) gave the annelated quinone **13a** (80% isolated) along with **14a** in a respective ratio of 23:1 (^{1}H NMR analysis). In contrast, thermolysis under like conditions except at higher concentrations (1.20 M) gave the corresponding quinones **13a** and **14a** in a respective ratio of 1:7 (^{1}H NMR) and in isolated yields of 8% and 62%. In an analogous study **9b** (2.43×10^{-3} M) gave **13b** in 57% yield and **14b** was not detected (^{1}H NMR) in the crude reaction mixture. At high concentration (0.10 M) **13b** and **14b** were obtained as a 1:1 mixture in 77% yield.

Thermolysis of **9c** shows analogous behavior when subjected to similar reaction conditions. That is, under high dilution (2.15×10^{-3} M) the quinone **13c** was isolated in 63% yield while **14c** was not detected. At a concentration of 0.7 M a 1:12 mixture of **13c** to **14c** was observed and the quinones were isolated in 4.2% and 66% yields, respectively.[4]

Formation of **13** is envisaged to arise in analogy to the formation of **6** except, of course, the ultimate diradical intermediate **12** abstracts a H-atom from the proximal hydroxy group. The rearrangements of **9** to **14** are further examples of the well-established ring expansion of 4-alkynyl-4-hydroxycyclobutenones to quinones, all of which are viewed as involving initial formation of the ketenes **10** and then the diradicals of structural type **11** as the ultimate precursors of the quinone products.[2,5-9] *The concentration dependence reveals that these diradicals 11 lead to quinones 14 via an inter- rather than an intramolecular H-atom transfer process.*[10]

Scheme III



Formation of **13c** is of further interest, particularly when compared to the rearrangement of **7b** to the chromanol **8b** (Scheme II). *Together, these results suggest a kinetic preference for 6-exo addition of the aryl radical center of the initially formed diradical to the alkynyl moiety over 1,5-H transfer from the propargylic position.*[11] With **9c** this leads to the ultimate diradical intermediate **12c** which undergoes facile termination via 1,5-H transfer from the adjacent hydroxyl group. With **7b** this pathway is either blocked on steric grounds or it is reversible since the terminating H-atom transfer step would be less favorable, i.e., 1,6- cf 1,5-H transfer. Thus, the aryl radical arising from **7b** ultimately undergoes 1,5-H transfer from the propargylic position which then leads to chromanol **8b**.

In conclusion, the following significant observations are reported: (1) a unique ring expansion of 4-alkynylcyclobutenones to highly functionalized spiroepoxides and/or quinones is described; (2) the rearrangements involve unusual diradical intermediates; and (3) the concentration dependence of the quinones synthesis establishes an intermolecular H-atom transfer in the previously reported ring expansion of 4-alkynyl-4-hydroxycyclobutenones.[2]

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Supplementary Material Available: Experimental procedures and compound characterization data (10 pages). This material is contained in many 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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(9) Enhsen, A.; Karabelas, K.; Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1990**, *55*, 1177.
(10) The analogous trimethylsilyl transfer leading to silylquinones has been shown to be an intramolecular process (ref 2). This was confirmed here in a study of the thermolysis of the 4-(trimethylsilyl)oxy derivative of **9a** which rearranged to the "normal" quinone and the reaction was observed to be concentration independent.
(11) Such a process is likely limited to aryl or alkenyl radicals since they are significantly more reactive than alkyl radicals toward cyclizations. See, for example: Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1985**, 4529. Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525.