

bicyclobutoniumion- d_2 ,¹⁰ where the EIE is an average of a large effect preferring deuterium in the low-field (endo)¹¹ position and a smaller one preferring deuterium in the upfield (exo)¹¹ position. The size of the isotope splitting in the ¹³C NMR spectrum of **1-d** corresponds to the arithmetic mean of the two isotope effects which are different in size and sign in the *exo*- and *endo*-C₄H₆D⁺ cations.¹⁰

Taking into account the adequate intensity/chemical shift ratio and the fundamental coincidence of the EIE's in **1** with those in the parent ion, it can be concluded that the minimum-energy structure for **1** is the methylbicyclobutonium ion structure **4**. At higher temperatures the degenerate equilibrium of three bicyclobutonium ions is principally perturbed to different sides by *endo* and *exo* deuterium (Scheme I). However, contrary to the C₄H₇⁺ cation, the geminal protons at the averaged methylene carbons are not distinct in C₄H₆CH₃⁺. Averaging of the geminal protons occurs by inversion via a planar cyclobutyl cation transition state,¹² thus leading to averaged *exo/endo* EIE's in the C₄H₆CH₃⁺ cation.

The *endo* C-H bond at the pentacoordinated carbon has a much lower bond force constant than the other *endo* proton bonds. Vibrations are less hindered because bridging drains electron density particularly out of this C-H bond.^{12,13} This resembles the transition state of an α primary KIE ($k_H/k_D > 1$) in an S_E2 reaction.¹⁴ The *endo* proton would be the leaving group and the bridging carbon the incoming electrophile. The reverse applies for the *exo* C-H bonds, which are to be more hindered to bending vibration due to crowding at the pentacoordinated carbon. This inverse effect can be compared with an α secondary KIE ($k_H/k_D < 1$).⁷

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Registry No. **1**, 96347-33-0; **2**, 14973-56-9; **3**, 19067-43-7; **4**, 96347-32-9; D₂, 7782-39-0; 1-methylcyclobutyl cation, 19394-14-0; (1-methylcyclopropyl)carbinyl cation, 27761-35-9.

(10) Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868.

(11) Brittain, W. J.; Squillacote, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 7280.

(12) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 6388.

(13) Cf.: Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.

(14) Cf.: Bencivenno, D. J.; Brownawell, M. L.; Li, M.-Y.; Filippo, J. S., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3703.

(2-Alkynylethenyl)ketenes: A New Benzoquinone Synthesis

J. Olle Karlsson, Nghi V. Nguyen, Lafayette D. Foland, and Harold W. Moore*

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

Received January 28, 1985

We wish to report the generation and chemistry of the heretofore unknown (2-alkynylethenyl)ketenes, specifically those of general structure **2**. Such compounds are accessible from the corresponding alkynylcyclobutenones **1**. The ketenes thus generated are envisaged to undergo ring closure to the unique zwitterions **3** and **4** and these, in turn, proceed to products **5** and **6** via transfer of the trimethylsilyl group.¹ Significantly, the formation of **5** constitutes a new and potentially general quinone synthesis.

The results of this study are outlined in Scheme I and Table I. The 4-alkynyl-2,3-dimethoxy-4-(trimethylsilyloxy)cyclobutenones **1a-e** were thermolyzed in refluxing *p*-xylene (135 °C) to give both five- and six-membered ring products. The ring closure pathway is influenced by the substituent R. Specifically, electron-with-

Scheme I

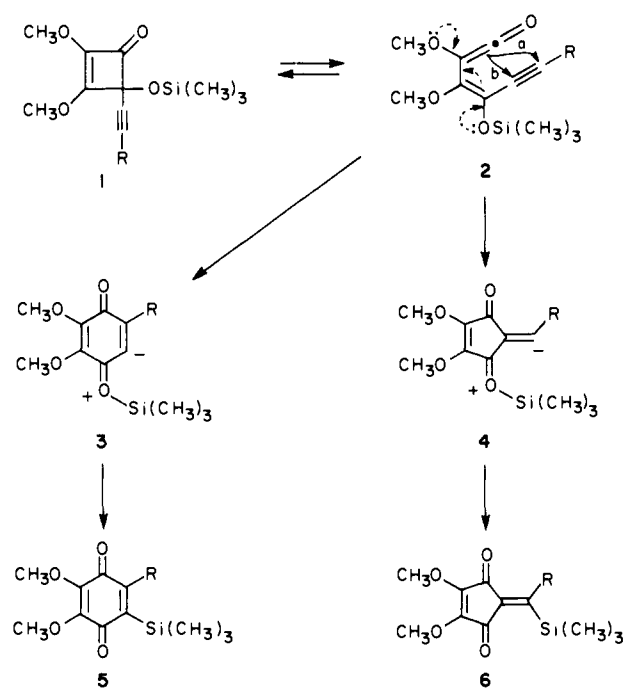


Table I

R	Isolated Yields (%)	
	5	6
a, CO ₂ C ₂ H ₅		33 ^a
b, C ₆ H ₅	13 ^b	52
c, <i>n</i> -C ₄ H ₉	75	
d, CH ₂ C ₆ H ₅	74	
e, CH ₂ OSi(CH ₃) ₃	80	

^aA yield of 43% was obtained starting from a chromatographed (silica gel) sample of the cyclobutenone **1a**. However, the yield of **1a** was only 21% after chromatography due to hydrolysis. ^b**5b** and **6b** could not be separated by chromatography; instead the mixture was reduced with sodium dithionite. The hydroquinone of **5b** was then separated from **6b** by chromatography and later reoxidized to **5b** with Ag₂O. The yield of **5b** is based on the isolated yield of its hydroquinone.

drawing groups favor the formation of cyclopentenediones **6** and electron-releasing groups favor the quinones **5**. The structures of these products are based upon spectral (Table II) and chemical properties. For example, the quinones **5b-e** all show a positive leucomethylene blue test and can be easily reduced to their corresponding hydroquinones upon treatment with sodium dithionite.

The proposed mechanism for the conversion of **1** to **5** and **6** is provided in Scheme I. The cyclobutenones **1** would be anticipated to be in equilibrium with the (2-alkynylethenyl)ketenes **2** at 135 °C. These ketenes are viewed as undergoing ring closure to **3** and/or **4**.^{2,3} As is indicated by the product distributions, the mode of ring closure (path a vs. path b) is dictated by the electronic influence of the alkyne substituent, R. Transfer of the trimethylsilyl group to the negative site then gives the products

(2) For a review, see: Marvell, E. N. "Thermal Electrocyclic Reactions"; Academic Press: New York, 1980; pp 124-190. See also, for example: Jackson, D. A.; Rey, M.; Dreiding, A. S. *Tetrahedron Lett.* **1983**, 4817. Berge, J. M.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 2230. Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc.* **1982**, *104*, 7670. Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 451. Dötz, K. H.; Trenkle, B.; Schubert, U. *Angew. Chem.* **1981**, *93*, 296. Danheiser, R. L.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4810.

(3) The cyclobutenone-vinylketene equilibrium has recently been elegantly utilized by Danheiser and Gee for the generation of transitory dienylketenes which cyclize to highly substituted phenols. See: Danheiser, R. L.; Gee, H. *J. Org. Chem.* **1984**, *49*, 1674.

(1) The corresponding diradical structure is also a viable possibility. See ref 5.

Table II. Physical Properties of Compounds 5 and 6^a

mp, °C	NMR (CDCl ₃), δ	IR, cm ⁻¹	MS
5b 89.5-90.5	7.5-6.9 (m, 5 H), 4.06 (s, 3 H), 3.98 (s, 3 H), -0.08 (s, 9 H)	2950 (m), 1655 (s), 1645 (s), 1630 (s), 1570 (m), 1450 (m), 1265 (s), 1245 (m), 1100 (s), 840 (s)	316 (43%, EI), 317 (60%, CI)
5c oil	4.00 (s, 3 H), 3.95 (s, 3 H), 2.54 (br t, 2H, J = 7 Hz), 1.5-1.2 (m, 4 H), 0.92 (brt, 3 H, J = 7 Hz), 0.30 (s, 9 H)	2940 (s), 1635 (s), 1575 (m), 1450 (m), 1240 (s), 1190 (m), 1110 (s), 1060 (s), 840 (s)	296 (68%, EI), 297 (91%, CI)
5d 59.5-60	7.5-6.9 (m, 5 H), 3.95 (s, 3 H), 3.90 (s, 2 H), 3.82 (s, 3 H), 0.32 (s, 9 H)	2920 (m), 1630 (s), 1525 (m), 1445 (m), 1245 (s), 1185 (m), 1115 (s), 1080 (m), 840 (s)	330 (7%, EI), 331 (100%, CI)
5e oil	4.47 (s, 2 H), 3.98 (s, 3 H), 3.97 (s, 3 H), 0.32 (s, 9 H), 0.14 (s, 9 H)	2940 (s), 1630 (s), 1580 (m), 1450 (m), 1310 (m), 1250 (s), 1190 (m), 1120 (s), 1080 (s), 840 (s)	342 (14%, EI), 343 (54%, CI)
5f oil	4.52 (brd, 2 H, J = 7 Hz), 4.02 (s, 3 H), 3.97 (s, 3 H), 2.49 (brt, 1 H, J = 7 Hz), 0.33 (s, 9 H)	3600-3100 (s), 2940 (s), 1660-1620 (s), 1580 (s), 1445 (s), 1250 (s), 1190 (s), 1120 (s), 1080 (s), 845 (s)	270 (10%, EI), 271 (15%, CI)
6a 68.5-69.5	¹ H (CDCl ₃) 4.36 (q, 2 H, J = 7 Hz), 4.27 (s, 6 H), 1.35 (t, 3 H, J = 7 Hz), 0.28 (s, 9 H); ¹ H (C ₆ D ₆) 4.32 (q, 2 H, J = 7 Hz), 3.62 (s, 3 H), 3.59 (s, 3 H), 1.18 (t, 3 H, J = 7 Hz), 0.44 (s, 9 H); ¹³ C (CDCl ₃) 184.9, 182.8, 170.6, 153.2, 151.8, 135.4, 61.1, 60.1, 60.0, 14.2, -1.3	2940 (m), 1720-1675 (s), 1630-1590 (s), 1430 (m), 1325 (s), 1215 (s), 1150 (s), 1090 (s), 1020 (m), 840 (s)	312 (7%, EI), 313 (16%, CI)
6b 95-95.5	¹ H (CDCl ₃) 7.4-7.2 (m, 3 H), 6.9-6.7 (m, 2 H), 4.25 (s, 3 H), 4.14 (s, 3 H), 0.11 (s, 9 H); ¹³ C (CDCl ₃) 186.3, 184.2, 163.5, 151.7, 151.6, 142.1, 134.2, 127.7, 126.2, 124.6, 59.9, 59.8, -0.4	2940 (w), 1675 (s), 1620 (s), 1460 (m), 1330 (s), 1070 (s), 835 (s)	316 (11%, EI), 317 (100%, CI)

^a Analytical data are all in agreement with the presented structures.

5 and 6. Such migration of a silyl moiety from oxygen to carbon is rare.⁴ However, here it is viewed as being a favorable transformation since such would result in the conversion of zwitterionic intermediates to neutral products. Finally it is noted that the suggested intermediates 3 and 4 are unique. Zwitterion 3 is of particular note since it can be considered as the polar form of a strained cyclic allene.⁵

The cyclobutenones 1a-e were readily prepared from dimethyl squarate.⁶ Thus, treatment of this ester with the pertinent lithium acetylde (-78 °C, THF) followed by quenching with trimethylsilyl chloride resulted in the formation of the cyclobutenones. The crude products were vacuum filtered through Florisil using hexanes-ethyl acetate mixtures to give the purified products in yields ranging from 72% to 88%. The hydrolytic lability of these products precluded their further purification. However, their spectral properties are in agreement with the assigned structures.⁷

The following experimental procedure for the conversion of 1c to 5c is typical. A 20-mL solution of 0.50 g of 1c in *p*-xylene was refluxed under argon for 2 h. During this time the initially colorless solution became dark orange. Analysis of the reaction mixture by TLC showed the presence of one major yellow product which gave an immediate blue spot (positive quinone test) upon treatment with leucomethylene blue solution. Removal of the solvent left a reddish oil. The product was purified by flash chromatography (silica gel, hexanes-ethyl acetate 9:1) to give 5c as a dark orange oil in 75% yield.

In conclusion, we wish to note the significant points of this study: (1) A general synthetic route to (2-alkynylethenyl)ketenes of structural type 2 from dimethyl squarate is now available. (2) Such ketenes readily undergo ring closure and this can be controlled to provide a unique and useful synthesis of trimethyl-

silyl-substituted quinones, a rare class of compounds.⁸ (3) The zwitterionic intermediates 3 and 4 are unique. (4) Finally it is noted that the formation of 5e is of particular interest since it suggests that propargyl alcohols can be utilized in a simple and potentially general route to quinones having those structural features deemed necessary for bioreductive alkylating agents.⁹

Acknowledgment. We thank the National Institutes of Health (CA-11890, AI-15651) and the National Science Foundation (CHE 80-25567) for financial support of this work.

(8) Hashimoto, T. *Yakugaku Zasshi* 1967, 87, 535. Bock, H.; Alt, H. *Angew. Chem., Int. Ed. Engl.* 1967, 6, 941. Razuvaev, G. A.; Vasileiskaya, N. S.; Gorbunova, L. V.; Chevnikova, G. V.; Bortnikov, G. N. *Izv. Akad. Nauk. SSSR Ser. Khim.* 1971, 20, 2392. Vasileiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Bortnikov, G. N. *Ibid.* 1972, 21, 2755. Vasileiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Makarenko, N. P.; Bortnikov, G. N. *Ibid.* 1975, 24, 2770.

(9) Moore, H. W.; Czerniak, R. *Med. Chem. Rev.* 1981, 1, 249.

Hydrolysis of Mustard Derivatives. Failure of the Raber-Harris Probe in Predicting Nucleophilic Assistance

S. P. McManus,* N. Neamati-Mazraeh, B. A. Hovanes, M. S. Paley, and J. M. Harris*

Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899

Received January 15, 1985

Several years ago Raber, Harris (RH), and co-workers¹ presented convincing evidence that nucleophilic solvent assistance could be detected by analysis of plots of solvolytic rates ($\log k$) of a substrate against those of 1-adamantyl bromide in aqueous ethanols and trifluoroethanols. A single correlation line was shown to be characteristic of substrates reacting by k_c and k_d mechanisms while separate aqueous ethanol and aqueous trifluoroethanol correlation lines were observed for k_s substrates. The method gave excellent predictions for several well-understood reactions, and upon application to controversial substrates,² predictions were made which agreed with a large body of data. Since then the RH

(4) Mora, J.; Costa, A. *Tetrahedron Lett.* 1984, 3493. Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *Organometallics* 1984, 3, 1583. Anderson, G.; Cameron, D. W.; Feutrill, G. I.; Read, R. W. *Tetrahedron Lett.* 1981, 4347.

(5) For example, earlier work has suggested that 1,2-cyclohexadiene may contain a planar zwitterionic structure (Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* 1970, 92, 5469. Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* 1975, 31, 1997. Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Ibid.* 1972, 28, 4883. Dillon, P. W., Underwood, G. R. *J. Am. Chem. Soc.* 1974, 96, 779). However, more recent investigations have cast doubt on that view and have predicted the diradical to be of lower energy than a zwitterion: Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* 1985, 107, 532. Balci, M.; Jones, W. M. *Ibid.* 1980, 102, 7607. Thus, intermediates 3 and 4 may be diradical rather than dipolar in character.

(6) Cohen, S.; Cohen, S. G. *J. Am. Chem. Soc.* 1966, 88, 1533.

(7) The possibility of 1,4-addition of the lithium reagent leading to 4-alkynyl-3,4-dimethoxy-2-(trimethylsilyloxy)cyclobutenone was ruled out from NMR spectral data. That is, both methoxy signals appear at approximately 4 ppm indicating that they are both situated on a double bond.

(1) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. M. *J. Am. Chem. Soc.* 1978, 100, 8137.

(2) Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* 1978, 100, 8147.