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REARRANGEMENTS OF CYCLOBUTENONES - CONVERSION OF SELECTED 4-ALLYLCYCLOBUTENONES TO BICYCLO[3.2.0]HEPTENONES

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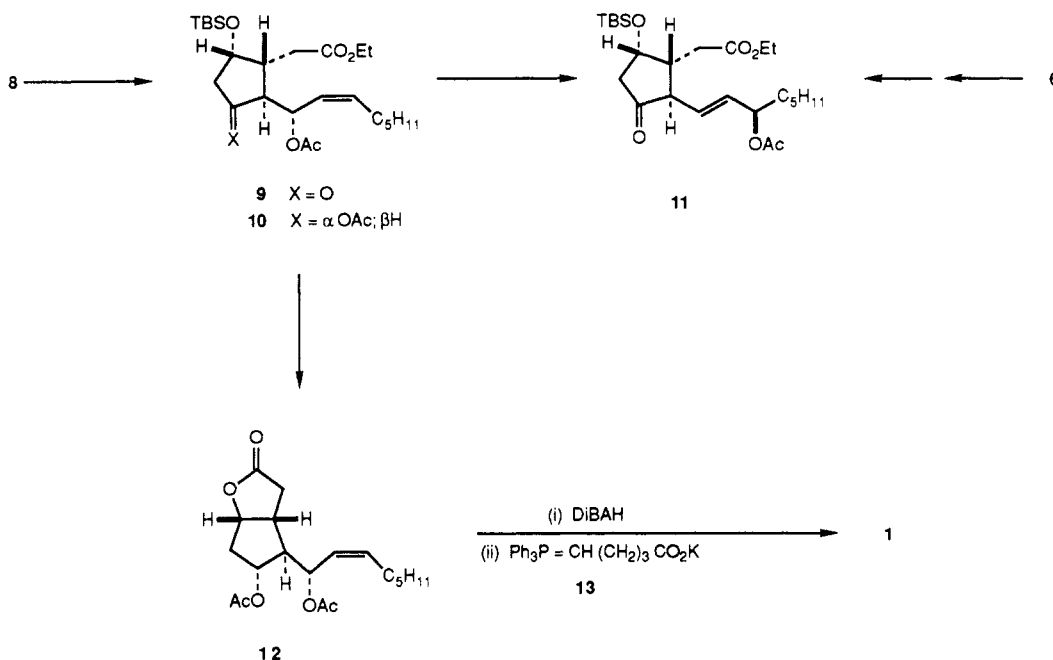
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Scheme III



from 12. The overall yield of 1 from 3 is 27%. As previously described, **3**^{5,12} is readily available in enantiomerically homogeneous form from *cis*-1,4-diacetoxycyclopentene.

The stereochemical outcome at C₁₃ arising from the coupling of similar substrates under the same conditions is amazing. In the previously described aldols⁵ leading to 5 and 6 no other stereoisomers were observed. Yet when the ynal 7 is employed 8 is the only product observed! Instead of offering ad hoc interpretations that do not flow from sound experimental observations, we prefer to outline an agenda of questions that must be addressed. Why does a particular substitution type on the aldehyde favor or disfavor silyl transfer? Is silyl transfer fundamental or accessory to the stereochemical outcome? Do the sharply differing results arise from a common transition-state

alignment differing in the placement of the R and H group of the aldehyde or do the reaction types differ in overall topography (chair vs boat, synclinal vs antiperiplanar)? Answers to these sorts of questions are not readily obtained but are crucial to illuminating this interesting stereochemical finding and extending it to new domains. *In the meantime, we note that the chemistry disclosed here and previously⁵ provides straightforward access to optically pure prostaglandins with complete control of the configuration at either C₁₃ or C₁₅ in any stereochemical sense.*

Acknowledgment. This research was supported by PHS Grant HL25848. NMR Spectra were obtained through the auspices of the Northeast Regional NSF/NMR facility at Yale University, which was supported by NSF Chemistry Division Grant CHE 7916210.

(12) Cf: (a) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* 1985, 5615. (b) Deardorff, D. R.; Matthews, A. J.; McMeekin, D. S.; Craney, C. L. *Ibid.* 1986, 1255.

Supplementary Material Available: Experimental procedures and characterization data for all compounds (5 pages). Ordering information is given on any current masthead page.

Rearrangements of Cyclobutenones. Conversion of Selected 4-Allylcyclobutenones to Bicyclo[3.2.0]heptenones

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Summary: 4-Allyl-4-alkoxy(or hydroxy or (trimethylsilyl)oxy)cyclobutenones are reported to rearrange to bicyclo[3.2.0]hept-2-en-7-ones upon thermolysis in refluxing toluene. The synthetic scope and mechanism of this unusual transformation are discussed. The products are envisaged to arise from an electrocyclic ring opening of the cyclobutenones to the corresponding vinylketenes which

then undergo an intramolecular [2 + 2] cycloaddition of the ketene moiety to the nonconjugated allylic double bond.

Sir: Selected 4-alkynyl, 4-alkenyl-, and 4-aryl cyclobutenones have recently been shown to undergo facile ring expansion to respectively benzoquinones, hydroquinones,

and annelated hydroquinones.¹⁻³ These transformations all have a mechanistic commonality in that the starting cyclobutenones experience a selective electrocyclic ring opening with outward rotation of the electron-donating group at 4-position to give the corresponding conjugated vinylketenes.⁴ These ketenes then undergo ring closure leading ultimately to the observed products. We now report that the corresponding nonconjugated vinylketenes can be generated from selected 4-allylcyclobutenones and these undergo facile intramolecular [2 + 2] cycloaddition of the ketene group to the nonconjugated allylic double bond, giving bicyclo[3.2.0]hept-2-en-7-ones.^{5,6} This is a synthetically useful reaction since the starting cyclobutenediones are readily prepared in a variety of substitution patterns, and, based upon analogy, the products are potentially versatile precursors to a number of other systems, including five-, six-, seven- and eight-membered rings.^{7,8}

(1) For the conversion of 4-alkynylcyclobutenones to quinones and 2-alkylidene-1,3-cyclopentenediones, see: (a) Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* 1985, 107, 3392. (b) Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* 1987, 52, 1174. (c) 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.

(2) For selected references to the conversion of 4-arylcyclobutenones to quinones, see: (a) Perri, S. T.; Foland, L. D.; Decker, O. H.; Moore, H. W. *J. Org. Chem.* 1986, 51, 3067. (b) Liebeskind, L. S.; Iyer, S.; Jewell, C. F. *J. Org. Chem.* 1986, 51, 3065. (c) Perri, S. T.; Moore, H. W. *Tetrahedron Lett.* 1987, 28, 4507. (d) Reed, M. W.; Moore, H. W. *J. Org. Chem.* 1988, 52, 4166. (e) Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* 1989, 111, 989.

(3) For the conversion of 4-alkenylcyclobutenones to quinones, see: (a) Perri, S. T.; Dyke, H. J.; Moore, H. W. *J. Org. Chem.* 1989, 54, 2032. (b) Perri, S. T.; Moore, H. W. *J. Am. Chem. Soc.*, in press.

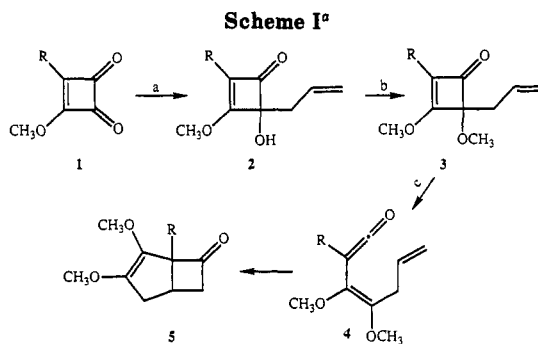
(4) The selectivity of the electrocyclic ring opening is in agreement with the computational studies reported for the analogous ring opening of cyclobutenes. See: (a) Houk, K. N.; Spellmeyer, D. G.; Jefford, C. W.; Rimbault, C. G.; Wang, Y.; Miller, R. D. *J. Org. Chem.* 1988, 53, 2125. (b) Randan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* 1985, 107, 2099.

(5) For an excellent review of intramolecular ketene/alkene cycloadditions, see: Snider, B. B. *Chem. Rev.* 1988, 88, 793.

(6) We are grateful to one of the reviewers who pointed out the recent independent study of the formation of a bicycloheptenone from 4,4-diallyl-2-methylcyclobutenone: Ernst, B.; de Mesmaeker, A.; Greuter, H.; Veenstra, S. J. In *Strain and its Implication in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Boston, 1989; pp 221-222.

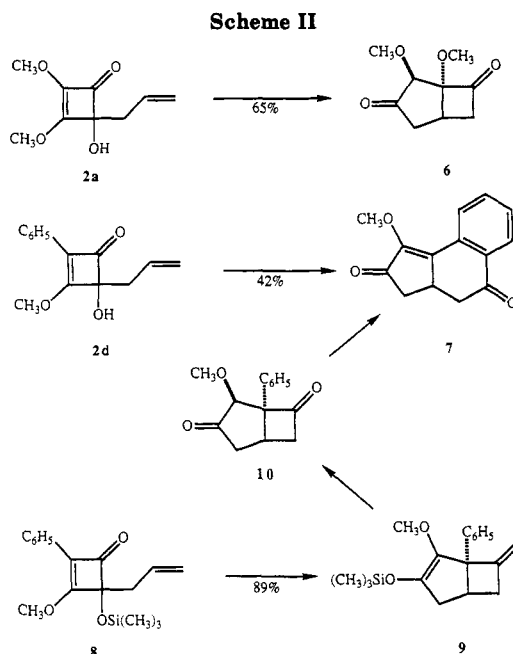
(7) For the conversion of squaric acid to substituted cyclobutenedione, see: (a) Reed, M. W.; Perri, S. T.; Pollart, D. J.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* 1988, 53, 2477. (b) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* 1988, 53, 2482. Also, a convenient synthesis of substituted benzocyclobutenediones has recently been reported. See: Liebeskind, L. S.; Lescosky, L. J.; McSwain, C. M. *J. Org. Chem.* 1989, 54, 1435.

(8) For selected examples of the conversion of bicyclo[3.2.0]heptanes to other ring systems, see the following. 5-membered ring systems: (a) Corey, E. J.; Kang, M.; Desai, M. C.; Ghosh, A. K.; Houpis, I. N. *J. Am. Chem. Soc.* 1988, 110, 649. (b) De Mesmaeker, A.; Veenstra, S. J.; Ernst, B. *Tetrahedron Lett.* 1988, 459. (c) Jackson, D. A.; Rey, M.; Dreiding, A. S. *Tetrahedron Lett.* 1983, 4817. (d) Matz, J. R.; Cohen, T. *Tetrahedron Lett.* 1981, 2459. (e) Wenkert, E.; Arrhenius, T. S. *J. Am. Chem. Soc.* 1983, 105, 2030. 6-membered ring systems: (f) Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem. Soc.* 1983, 105, 520. (g) Bhupathy, M.; Cohen, T. *J. Am. Chem. Soc.* 1983, 105, 6978. (h) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* 1981, 37, 3943. (i) Snider, B. B.; Niwa, M. *Tetrahedron Lett.* 1988, 3175. 7-membered ring systems: (j) Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* 1982, 65, 451. (k) Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* 1982, 65, 1563. (l) Hwang, C. S.; Reusch, W. *Synthesis* 1989, 428. (m) Oppolzer, W.; Wylie, R. D. *Helv. Chim. Acta* 1980, 63, 1198. (n) Imafuku, K.; Arai, K. *Synthesis* 1989, 501. 8-membered ring systems: (o) Gadwood, R. C.; Lett, R. M. *J. Org. Chem.* 1982, 47, 2268. (p) Gadwood, R. C.; Lett, R. M.; Wissinger, J. E. *J. Am. Chem. Soc.* 1986, 108, 6343. (q) Paquette, L. A.; Colapret, J. A.; Andrews, D. R. *J. Org. Chem.* 1985, 50, 201. (r) Birch, A. M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* 1980, 1195. Norbornene ring system: (s) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* 1978, 479.



R	% 2	% 3	% 5
a —OCH ₃	71	89	83
b —n-C ₄ H ₉	27	89	85
c —CH=CH ₂	53	87	90
d —C ₆ H ₅	58	95	86
e —n-C ₄ H ₉	42	80	72

^a (a) Allylmagnesium bromide/THF, -100 °C; (b) CH₃I, Ag₂O, K₂CO₃/CH₃CN, room temperature; (c) toluene, 110 °C.



Specific examples of this transformation are given in Scheme I. The starting cyclobutenediones 1a-e were converted to the corresponding 4-allyl-3,4-dimethoxycyclobutenones 3a-e upon treatment with allylmagnesium bromide followed by O-alkylation of the resulting 4-hydroxycyclobuten-1-ones 2a-e with methyl iodide.⁹ Thermolysis of 3a-e in refluxing toluene then gave the bicyclo[3.2.0]heptenones 5a-e in excellent yields via the proposed ketene intermediates 4a-e. The structure assignments of 5a-e as well as of 2a-e and 3a-e are based upon characteristic spectral data which are provided in Table I.

Additional examples of this unusual ring expansion are given in Scheme II. For example, it was of interest to see

(9) Treatment of dimethyl squarate 1a with Grignard reagents has previously been reported to give 1,4-addition rather than 1,2-adducts. see: Kraus, J. L. *Tetrahedron Lett.* 1985, 26, 1867. However, with allylmagnesium bromide, as noted here, the reaction proceeds to give the 1,2-adduct 2a (71%) along with the diadduct in which allyl groups have added to both carbonyl moieties (15%).

Table I. Physical Properties of Compounds 2-10^{a,b}

compd	mp, °C	NMR (CDCl ₃), δ	IR, cm ⁻¹	MS
2a	34-37	¹ H 2.44 (s, 1 H), 2.61 (d, <i>J</i> = 9.0 Hz, 1 H), 3.96 (s, 3 H), 4.14 (s, 3 H), 5.19 (d, <i>J</i> = 12.0 Hz, 1 H), 5.21 (d, <i>J</i> = 15.0 Hz, 1 H), 5.78-5.93 (m, 1 H); ¹³ C 37.51, 58.30, 60.00, 85.50, 119.00, 131.92, 133.51, 167.95, 186.81	3380, 3020, 2960, 1780, 1630, 1470, 1440, 1350, 1240, 1050, 1000, 930, 890, 870	185 (100, CI)
2b	oil	¹ H 0.89 (t, <i>J</i> = 7.5 Hz, 3 H), 1.26-1.38 (m, 2 H), 1.43-1.54 (m, 2 H), 2.04-2.15 (m, 2 H), 2.58 (dd, <i>J</i> = 14.1, 7.4 Hz, 1 H), 2.67 (dd, <i>J</i> = 14.1, 7.4 Hz, 1 H), 2.77 (s, 1 H), 4.12 (s, 3 H), 5.13-5.23 (m, 2 H), 5.73-5.87 (m, 1 H); ¹³ C 13.54, 21.42, 22.32, 29.57, 37.61, 59.22, 90.39, 118.67, 127.17, 132.09, 183.43, 193.82	3460, 2970, 2940, 2880, 1760, 1750, 1620, 1610, 1465, 1360, 1090, 1000, 920	210 (3, EI)
2c	oil	¹ H 2.58-2.73 (m, 2 H), 4.19 (s, 3 H), 5.15-5.25 (m, 2 H), 5.39 (dd, <i>J</i> = 11.0, 2.0 Hz, 1 H), 5.76-5.90 (m, 1 H), 5.96 (dd, <i>J</i> = 17.6, 2.0 Hz, 1 H), 6.18 (dd, <i>J</i> = 18.0, 11.0 Hz, 1 H); ¹³ C 37.88, 60.03, 90.73, 119.26, 121.51, 121.71, 123.35, 131.71, 180.70, 191.09	3380, 2980, 1760, 1750, 1650, 1590, 1470, 1360, 1090, 1000, 930, 740	181 (100, CI)
2d	101-104	¹ H 2.73 (ddt, <i>J</i> = 14.2, 7.2, 1.0 Hz, 1 H), 2.85 (s, 1 H), 2.87 (ddt, <i>J</i> = 14.2, 7.6, 1.0 Hz, 1 H), 4.27 (s, 3 H), 5.15-5.30 (m, 2 H), 5.78-5.92 (m, 1 H), 7.26-7.40 (m, 3 H), 7.70-7.73 (m, 2 H); ¹³ C 38.53, 59.98, 92.11, 119.20, 124.07, 126.91, 128.00, 128.24, 128.33, 131.79, 181.94, 190.95	3330, 3000, 1760, 1635, 1600, 1500, 1470, 1450, 1370, 1320, 1010, 1000, 690	231 (100, CI)
2e	57-58	¹ H 0.91 (t, <i>J</i> = 7.2 Hz, 3 H), 1.40-1.60 (m, 4 H), 2.33 (t, <i>J</i> = 7.0 Hz, 2 H), 2.60 (d, <i>J</i> = 7.4 Hz, 2 H), 2.67 (s, 1 H), 4.33 (s, 3 H), 5.17-5.25 (m, 2 H), 5.76-5.90 (m, 1 H); ¹³ C 13.46, 19.11, 21.91, 30.23, 37.32, 60.76, 66.91, 90.09, 95.46, 108.22, 119.38, 131.30, 184.60, 190.07	3370, 2960, 2940, 2880, 2240, 1770, 1615, 1460, 1360, 1240, 990, 930, 640	235 (100, CI)
3a	oil	¹ H 2.54 (dd, <i>J</i> = 14.4, 7.5 Hz, 1 H), 2.63 (dd, <i>J</i> = 14.4, 7.2 Hz, 1 H), 3.33 (s, 3 H), 3.97 (s, 3 H), 4.12 (s, 3 H), 5.10-5.15 (m, 1 H), 5.70-5.84 (m, 1 H); ¹³ C 36.51, 51.81, 58.28, 59.69, 91.42, 118.25, 132.01, 134.59, 167.03, 185.89	2990, 2960, 2840, 1780, 1650, 1470, 1440, 1350, 1225, 1140, 1120, 1055, 1020, 1000, 950, 930, 890, 850	199 (100, CI)
3b	oil	¹ H 0.90 (t, <i>J</i> = 7.2 Hz, 3 H), 1.30-1.40 (m, 2 H), 1.45-1.55 (m, 2 H), 2.10-2.16 (m, 2 H), 2.51 (ddt, <i>J</i> = 14.4, 7.6, 1.0 Hz, 1 H), 2.69 (ddt, <i>J</i> = 14.4, 7.0, 1.2 Hz, 1 H), 3.34 (s, 3 H), 4.10 (s, 3 H), 5.06-5.17 (m, 2 H), 5.65-5.79 (m, 1 H); ¹³ C 13.51, 21.45, 22.39, 29.72, 36.92, 52.38, 58.98, 96.71, 118.28, 129.15, 132.19, 182.44, 191.79	2970, 2950, 2880, 1770, 1635, 1625, 1470, 1460, 1360, 1290, 1120, 1000, 930	224 (7, EI)
3c	oil	¹ H 2.55 (ddt, <i>J</i> = 14.4, 7.6, 1.0 Hz, 1 H), 2.71 (ddt, <i>J</i> = 14.4, 7.0, 1.2 Hz, 1 H), 3.36 (s, 3 H), 4.16 (s, 3 H), 5.07-5.18 (m, 2 H), 5.40 (dd, <i>J</i> = 11.0, 2.1 Hz, 1 H), 5.69-5.83 (m, 1 H), 5.97 (dd, <i>J</i> = 17.6, 2.1 Hz, 1 H), 6.17 (dd, <i>J</i> = 17.6, 11.0 Hz, 1 H); ¹³ C 37.10, 52.80, 59.78, 96.97, 118.60, 121.40, 121.67, 124.84, 131.83, 180.23, 189.86	3000, 2960, 2840, 1760, 1650, 1590, 1470, 1460, 1410, 1360, 1300, 1140, 1120, 1000, 930	194 (3, EI)
3d	oil	¹ H 2.64 (ddt, <i>J</i> = 14.5, 7.7, 1.0 Hz, 1 H), 2.90 (ddt, <i>J</i> = 14.5, 7.0, 1.3 Hz, 1 H), 3.43 (s, 3 H), 4.23 (s, 3 H), 5.08-5.23 (m, 2 H), 5.71-5.85 (m, 1 H), 7.26-7.36 (m, 3 H), 7.75-7.80 (m, 2 H); ¹³ C 37.87, 52.91, 59.73, 98.37, 118.84, 125.54, 126.97, 128.06, 128.15, 128.42, 131.83, 181.16, 188.97	3000, 2960, 2840, 1760, 1630, 1600, 1500, 1365, 1340, 1320, 1140, 1120, 1100, 1000, 790, 700, 620	244 (13, EI)
3e	oil	¹ H 0.91 (t, <i>J</i> = 7.2 Hz, 3 H), 1.38-1.60 (m, 4 H), 2.35 (t, <i>J</i> = 6.9 Hz, 2 H), 3.34 (s, 3 H), 4.33 (s, 3 H), 5.10-5.18 (m, 2 H), 5.69-5.83 (m, 2 H); ¹³ C 13.50, 19.18, 21.97, 30.28, 36.48, 53.02, 60.59, 66.77, 95.67, 96.55, 109.72, 118.83, 131.59, 184.73, 189.57	2970, 2940, 2240, 1775, 1650, 1640, 1470, 1460, 1360, 1130, 990, 930, 720	248 (9, EI)
5a	oil	¹ H 2.30 (d, <i>J</i> = 16.2 Hz, 1 H), 2.55-2.70 (m, 2 H), 2.90 (dd, <i>J</i> = 16.2, 7.0 Hz, 1 H), 3.10 (dd, <i>J</i> = 17.4, 9.1 Hz, 1 H), 3.32 (s, 3 H), 3.68 (s, 3 H), 3.81 (s, 3 H); ¹³ C 26.29, 32.74, 47.89, 52.21, 57.19, 58.34, 103.30, 127.54, 142.10, 203.85	2990, 2960, 2860, 1785, 1770, 1680, 1470, 1460, 1300, 1260, 1235, 1150, 1100, 1075, 1020, 1000, 800	170 (19, EI)
5b	oil	¹ H 0.90 (t, <i>J</i> = 7.2 Hz, 3 H), 1.20-1.35 (m, 4 H), 1.65-1.75 (m, 2 H), 2.30 (d, <i>J</i> = 15.4 Hz, 1 H), 2.30-2.38 (m, 1 H), 2.60 (dd, <i>J</i> = 15.7, 8.1 Hz, 1 H), 2.89 (dd, <i>J</i> = 18.1, 5.6 Hz, 1 H), 3.18 (dd, <i>J</i> = 17.9, 8.6 Hz, 1 H), 3.65 (s, 3 H), 3.71 (s, 3 H); ¹³ C 13.89, 22.87, 25.07, 26.34, 28.15, 33.18, 51.07, 57.24, 58.79, 77.44, 131.60, 138.12, 209.98	2960, 2940, 2860, 1780, 1675, 1465, 1390, 1335, 1290, 1255, 1230, 1220, 1160, 1090, 1080, 1025, 1000	224 (3, EI)
5c	oil	¹ H 2.33 (d, <i>J</i> = 15.7 Hz, 1 H), 2.45-2.53 (m, 1 H), 2.85-2.96 (m, 2 H), 3.27 (dd, <i>J</i> = 18.1, 9.1 Hz, 1 H), 3.64 (s, 3 H), 3.74 (s, 3 H), 5.25 (d, <i>J</i> = 10.7 Hz, 1 H), 5.38 (d, <i>J</i> = 16.1 Hz, 1 H), 5.97 (dd, <i>J</i> = 17.5, 10.7 Hz, 1 H); ¹³ C 27.49, 32.75, 50.98, 57.26, 58.85, 78.71, 116.68, 131.63, 133.12, 138.53, 206.67	2980, 2940, 2850, 1780, 1770, 1680, 1465, 1455, 1340, 1300, 1260, 1240, 1100, 1000, 930	194 (20, EI)
5d	oil	¹ H 2.42 (d, <i>J</i> = 15.9 Hz, 1 H), 2.62-2.66 (m, 1 H), 3.00-3.07 (m, 2 H), 3.35 (dd, <i>J</i> = 18.1, 9.2 Hz, 1 H), 3.53 (s, 3 H), 3.78 (s, 3 H), 7.26-7.39 (m, 5 H); ¹³ C 29.90, 33.07, 51.47, 57.42, 59.05, 79.73, 126.20, 127.25, 128.55, 132.64, 137.81, 139.20, 206.68	2960, 2860, 1775, 1680, 1500, 1450, 1395, 1340, 1310, 1260, 1240, 1080, 760, 700	244 (HR)
5e	oil	¹ H 0.88 (t, <i>J</i> = 7.5 Hz, 3 H), 1.33-1.51 (m, 4 H), 2.20-2.30 (m, 3 H), 2.55-2.61 (m, 1 H), 2.91 (dd, <i>J</i> = 15.7, 8.1 Hz, 1 H), 2.98 (dd, <i>J</i> = 18.3, 5.9 Hz, 1 H), 3.35 (dd, <i>J</i> = 18.3, 9.2 Hz, 1 H), 3.70 (s, 3 H), 3.73 (s, 3 H); ¹³ C 13.55, 18.74, 21.88, 29.21, 30.64, 33.01, 52.14, 57.31, 59.03, 68.80, 74.02, 89.36, 129.99, 138.42, 201.85	2970, 2950, 2870, 1790, 1680, 1470, 1400, 1340, 1300, 1260, 1230, 1180, 1100, 1075, 1030, 1000	249 (100, CI)
6	79-82	¹ H 2.45 (dd, <i>J</i> = 18.4, 6.7 Hz, 1 H), 2.53 (d, <i>J</i> = 17.4 Hz, 1 H), 2.92-3.14 (m, 2 H), 3.18-3.27 (m, 1 H), 3.49 (s, 3 H), 3.56 (s, 3 H), 4.12 (s, 1 H); ¹³ C 27.53, 41.55, 46.79, 53.69, 88.01, 101.70, 201.73, 209.36	3040, 3020, 2970, 2940, 2840, 1790, 1765, 1465, 1400, 1300, 1240, 1160, 1130, 1100, 1025, 650	156 (5, EI)
7	139-141	¹ H 2.27 (dd, <i>J</i> = 18.7, 3.0 Hz, 1 H), 2.53 (dd, <i>J</i> = 15.8, 14.1 Hz, 1 H), 2.79 (dd, <i>J</i> = 18.7, 6.5 Hz, 1 H), 3.08 (dd, <i>J</i> = 15.8, 3.0 Hz, 1 H), 3.33-3.43 (m, 1 H), 4.17 (s, 3 H), 7.50 (td, <i>J</i> = 9.3, 1.2 Hz, 1 H), 7.65 (td, <i>J</i> = 8.1, 1.2 Hz, 1 H), 8.13 (d, <i>J</i> = 6.3 Hz, 1 H), 8.58 (d, <i>J</i> = 7.8 Hz, 1 H); ¹³ C 33.39, 40.31, 45.27, 58.37, 127.56, 128.27, 130.05, 131.75, 134.00, 134.90, 143.86, 151.46, 195.65, 200.97	3040, 3020, 2960, 1710, 1700, 1625, 1600, 1450, 1370, 1330, 1290, 1260, 1135, 1085, 985, 800	228 (89, EI)

Table I (Continued)

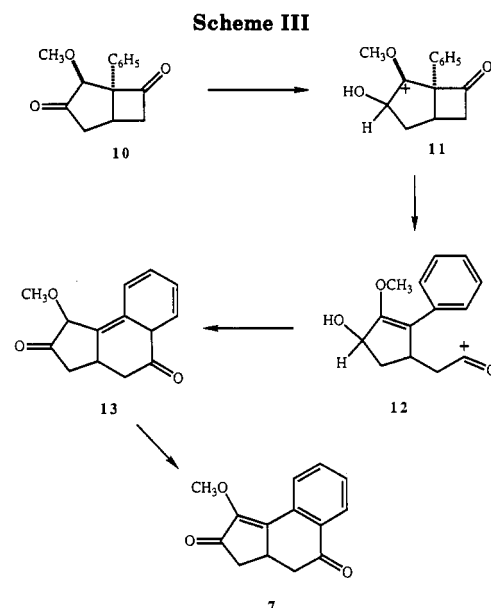
compd	mp, °C	NMR (CDCl ₃), δ	IR, cm ⁻¹	MS
8	oil	¹ H 0.18 (s, 9 H), 2.62 (dd, <i>J</i> = 14.4, 7.8 Hz, 1 H), 2.85 (dd, <i>J</i> = 14.4, 6.9 Hz, 1 H), 4.24 (s, 3 H), 5.07 (d, <i>J</i> = 10.0 Hz, 1 H), 5.15 (dd, <i>J</i> = 17.0, 1.4 Hz, 1 H), 5.68–5.76 (m, 1 H), 7.25–7.37 (m, 3 H), 7.72–7.74 (m, 2 H); ¹³ C 40.06, 59.63, 93.96, 118.60, 126.88, 127.93, 128.43, 132.22, 181.86, 189.02	2960, 1760, 1630, 1600, 1500, 1450, 1370, 1260, 1120, 1000, 930, 890, 850, 770, 760, 700	302 (8, EI)
9	oil	¹ H 0.26 (s, 9 H), 2.29 (d, <i>J</i> = 16.0 Hz, 1 H), 2.57–2.62 (m, 1 H), 2.93 (dd, <i>J</i> = 15.5, 7.5 Hz, 1 H), 3.02 (dd, <i>J</i> = 18.0, 5.5 Hz, 1 H), 3.35 (dd, <i>J</i> = 18.0, 9.0 Hz, 1 H), 3.51 (s, 1 H), 7.24–7.27 (m, 2 H), 7.32–7.38 (m, 3 H); ¹³ C 0.55, 30.45, 36.35, 51.50, 58.32, 79.14, 126.16, 127.19, 128.57, 134.48, 134.96, 138.05, 206.83	2970, 2920, 2860, 1770, 1680, 1400, 1450, 1390, 1340, 1300, 1250, 1100, 1075, 930, 870, 850, 760, 700	303 (100, CI)
10	oil	¹ H 2.63 (d, <i>J</i> = 17.9 Hz, 1 H), 2.89 (dd, <i>J</i> = 17.9, 5.1 Hz), 1 H), 3.06 (dd, <i>J</i> = 17.6, 7.7 Hz, 1 H), 3.27–3.50 (m, 2 H), 3.54 (s, 3 H), 4.01 (s, 1 H), 7.31–7.48 (m, 5 H)	2980, 2920, 2840, 1780, 1760, 1600, 1490, 1450, 1410, 1390, 1210, 1140, 1130, 1080, 1050, 1040, 760, 700	230 (7, EI)

^a Elemental analysis data for **2a**, **2d**, **2e**, **6**, and **7** are in accord with the proposed structures. ^b High-resolution mass spectra data for all compounds are in accord with the proposed structures.

if the direct precursors to **3**, i.e., 4-allyl-4-hydroxycyclobutenones, would undergo analogous ring expansion and thus provide a regioselective route to bicyclo[3.2.0]heptane-3,6-diones. To this end, the thermolysis of **2a** (toluene) was investigated and gratifyingly the bicycloheptanedione **6** was isolated in 65% yield. Nuclear magnetic resonance analysis of the crude reaction mixture showed the presence of the diastereomer of **6** as a minor product, and this could be converted to **6** upon treatment with silica gel. The structure of **6** is based upon standard spectral data (Table I) as well as upon a complete X-ray crystallographic structure determination, which clearly reveals the methoxy groups to be *trans* to one another.

The above synthesis of bicyclo[3.2.0]heptanediones is limited in scope as shown by the fact that the 2-substituent of the starting cyclobutenones plays a dominant role in the course of the reaction. In this regard, 4-allyl-4-hydroxy-3-methoxy-2-phenylcyclobutenone (**2d**) did not give a bicycloheptanedione as an isolatable product but rather gave **7** (42%) when subjected to the same reaction conditions used for the conversion of **2a** to **6**.¹⁰ This is a particularly unusual transformation and involves an overall dehydrogenation in addition to the molecular reorganization.

Evidence concerning the mechanism of the conversion of **2d** to **7**, as well as an example extending the synthetic scope of the allylcyclobutenone rearrangement, was obtained from an investigation of the thermolysis of 4-allyl-3-methoxy-2-phenyl-4-((trimethylsilyloxy)cyclobutenone (**8**). Here, a high yield (89%) of the bicycloheptenone **9** was realized. Desilylation of **9** upon treatment with CsF gave **10** (71%) as a 8:1 mixture of diastereomers. It was found that **10** was stable when subjected to the thermolysis in refluxing toluene (conditions used for the rearrangement of **2d** to **7**) but was converted to **7** (31%) in refluxing toluene in the presence of a few drops of glacial acetic acid.¹¹ This transformation is envisaged to involve the initial formation of the bicycloheptanedione **10**, which then undergoes an acid-catalyzed 1,3-acyl group migration to give **13** via the carbocation intermediates **11** and **12**.¹² Dehydrogenation of **13** and/or one of its possible tautomeric isomers under the reaction conditions would then



provide the observed product **7** (Scheme III). Presumably, the thermolysis of **2d** results in the formation of **10** and that sufficient acid is also generated to induce the rearrangement of **10** to **7**.

In summary, 4-allyl-4-alkoxy(or hydroxy or silyloxy)cyclobutenones, available in a variety of substitution patterns, rearrange to bicyclo[3.2.0]heptenones in good to excellent yields upon thermolysis in refluxing toluene. It is noted that the bicyclo[3.2.0]hept-2-en-7-one ring system is rare, particularly in highly functionalized forms.⁵ Clearly, its synthesis as outlined here has advantages over other known methods. Also, this transformation complements earlier reports describing the ring expansion of appropriately substituted cyclobutenones to quinones, hydroquinones, annelated hydroquinones, and 2-alkylidene-1,3-cyclopentenediones.^{1-3,13}

Extension of these studies to include the intramolecular ketene cycloadditions to substituted allylic groups as well as to higher homologues will be reported in due course.

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(10) The structure of **7** is based upon the spectral data given in Table I as well as upon a complete X-ray crystallographic analysis.

(11) Two other products, tentatively assigned as 2-methoxy-3-phenyl-4-methylcyclopentenones and 2-methoxy-3-phenyl-5-methylcyclopentenone, were also isolated in 15% and 12% yields.

(12) Previously reported 1,3-acyl group migrations in the bicyclo[3.2.0]heptanone series have been reported but require high temperature or photolysis. See, for example: (a) Bertrand, M.; Gill, G.; Junino, A.; Maurin, R. *Tetrahedron Lett.* 1977, 1779. (b) Lyle, T. A.; Frei, B. *Helv. Chim. Acta* 1981, 64, 2598. (c) Lyle, T. A.; Mereyala, H. B.; Pasual, A.; Frei, B. *Helv. Chim. Acta* 1984, 67, 774.

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