

BRIDGED DIENES: SYNTHESIS OF BICYCLO[4.3.1]DECA-1,5-DIENE¹

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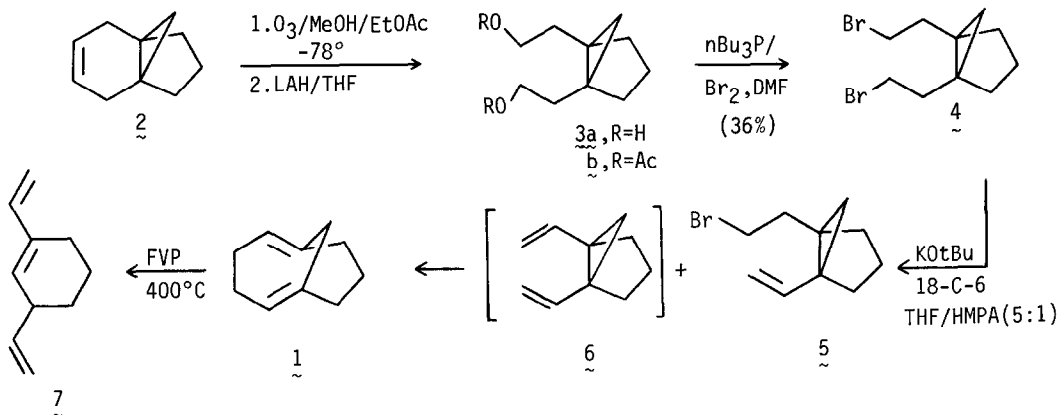
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Abstract: The title compound has been synthesized in several steps from [4.3.1]propell-3-ene; it thermally provides 1,3-divinylcyclohexene.

Our interest in bridgehead olefins² has led us to investigate bicyclic systems containing two such double bonds, termed bridged dienes.³ We recently reported⁴ the intermediacy of a trio of such dienes, and now relate the synthesis of one of them, and a derivative of another.

The synthesis of the title compound (**1**) proceeded from [4.3.1]propell-3-ene (**2**)⁵ (Scheme 1). Careful ozonolysis at -78°C, followed by LAH reduction, gave a 70% yield of diol **3a**.^{6a} The derived diacetate, **3b**,^{6b} proved quite stable (no thermolysis products below 580°C). After several thwarted attempts, access to dibromide **4**^{6c} was gained via treatment

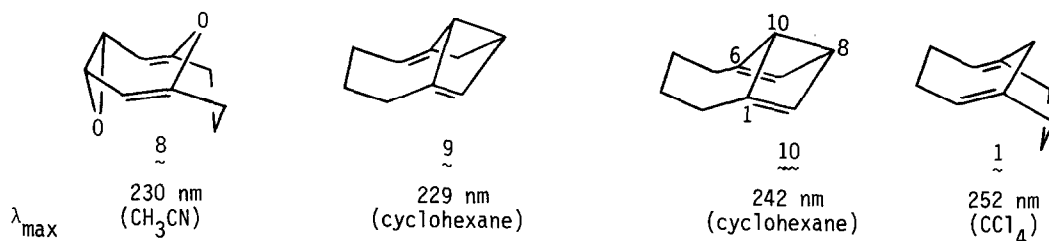
SCHEME I



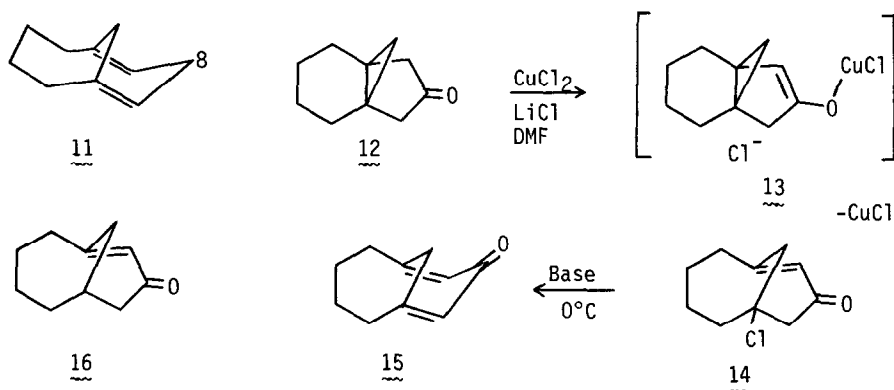
of **3a** with nBu₃PBr₂ in DMF. Satisfactory bisdehydrobromination of **4** also proved elusive; the t-BuO⁻/18-C-6 procedure afforded **1**⁷ in ca. 50% yield, with by-product **5**^{6d} as a contaminant.

The desired 1 was most easily purified via extraction with aqueous AgNO_3 solution, liberation with NH_4OH , and finally bulb-to-bulb distillation under high vacuum. The resulting diene (1) gave 1,3-divinylcyclohexene (7) upon flash vacuum pyrolysis at 400°C ; 7 had previously been found as a product in a reaction where the intermediacy of 1 was postulated.⁴ No spectroscopic evidence (PMR or CMR) for 6 could be adduced between -20° and 35°C .

It is of interest to compare the UV absorption maxima of 1, and related compounds 8,^{3c} 9,^{3e} and 10.^{3e} The apparent degree of interaction in 1 is greater than in 8; possibly the CH_2 bridge is more restrictive than the oxygen bridge. One would have to assume that the



double bonds of 1 are even more pyramidalized than those of 8.^{3b} That 1 would show more transannular π -interaction than 10 may initially be unexpected. However, an examination of models reveals that the $\text{C}_8\text{-C}_{10}$ bond in 10 causes a widening of the $\text{C}_1\text{-C}_6$ gap of about 6-9%, the result of which is the diminished π -overlap.



Of the rational approached to the more strained⁸ 11, it was hoped that placement of a carbonyl group at C₈ would both allow appropriate functionalization, and direct and facilitate elimination. In an attempt to α -chlorinate⁹ 12,¹⁰ access to chloroenone 14¹¹ was instead gained. This compound is similar to the known parent enone, 16.¹² The enolate route (cf. 13) was supported by the observation that chlorination of $\alpha,\alpha,\alpha',\alpha'$ -12-d₄ (using cupric chloride hydrate) afforded 14 without any deuterium.

Treatment of 14 with Et₃N¹² gave no reaction below 120°C; above 120°C decomposition occurred. However, reaction of 14 with NaH/DMF or LDA/ether gave an oil which was quite sensitive to silica gel, but was nearly purified by rapid thin layer chromatography. The spectral properties¹³ are consistent with 15, although further work will be necessary to confirm that assignment.

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References and Notes

1. This work was supported, in part, by the NSF (CHE-7618701).
2. (a) P. Warner, M. Ah-King and R. F. Palmer, *J. Am. Chem. Soc.*, **104**, 7166 (1982); (b) P. Warner and R. F. Palmer, *ibid.*, **103**, 1584 (1981); (c) P. Warner, S.-C. Chang, D. Powell and R. A. Jacobson, *ibid.*, **102**, 5125 (1980); (d) P. Warner, S. Lu, E. Myers, P. DeHaven and R. A. Jacobson, *ibid.*, **99**, 5102 (1977); (e) P. Warner, R. F. Palmer and S. Lu, *ibid.*, **99**, 3773 (1977).
3. (a) J. R. Wiseman and J. J. Vanderbilt, *ibid.*, **100**, 7730 (1978); (b) W. H. Rastetter, T. J. Richard, J. Bordner and G. L. Hennessee, *J. Org. Chem.*, **44**, 999 (1979); (c) W. H. Rastetter and T. J. Richard, *J. Am. Chem. Soc.*, **101**, 3893 (1979); (d) K. J. Shea and S. Wise, *Tetrahedron Lett.*, 2283 (1978); (e) L. A. M. Turkenburg, J. W. Van Straten, W. H. de Wolf and F. Bickelhaupt, *J. Am. Chem. Soc.*, **102**, 3256 (1980); (f) R. L. Viavattene, F. D. Green, L. D. Cheung, R. Majeste and L. M. Trefonas, *ibid.*, **96**, 4342 (1974); (g) K. B. Wiberg, M. Matturro and R. Adams, *ibid.*, **103**, 1600 (1981); (h) see also a review by K. J. Shea, *Tetrahedron, Rep. No. 85*, **36**, 1683 (1980).
4. P. Warner and W. Boulanger, *Tetrahedron Lett.*, **21**, 123 (1980).
5. E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer and H. Günther, *Liebigs Ann. Chem.*, **759**, 1 (1972).
6. (a) 3a: pmr (CCl₄): δ 3.80 (t, 4H, J=6.5 Hz), 2.3 (br s, 2H, OH), 1.2-2.1 (m, 10H), 0.55, 0.06 (AB, 2H, J=5); cmr (CDCl₃): δ 61.9, 36.0, 32.2, 28.5, 20.3, 16.9; ir (CCl₄): 3625, 3400, 1055, 1035, 1015 cm⁻¹. Anal.: calcd. for C₁₀H₁₈O₂-H₂O (P⁺ too weak for exact mass measurement): m/e 152.1201; found: 152.1200; (b) 3b: pmr (CCl₄): δ 4.14 (t, 4H, J=7) 2.0 (S, 6H), 1.2-2.3 (m, 10H), 0.52, 0.04 (AB, 2H, J=5); cmr (CDCl₃): δ 170.5, 75.6, 63.3,

31.9, 28.9, 20.6, 20.0, 16.5; ir (CCl₄): 1740, 1240, 1030 cm⁻¹. Anal. calcd. for C₁₄H₂₂O₄: C, 66.14%; H, 8.66%; found: C, 65.85%; H, 8.44%; (c) 4: pmr (CCl₄): δ 3.4 (t, 4H, J=8), 1.2-2.4 (m, 10H), 0.63, 0.02 (AB, 2H, J=5); cmr (CDCl₃): δ 37.0, 31.6, 31.3, 30.3, 20.1, 17.3; gcms: m/e 294, 296, 298 (P⁺ ions). A correct analysis was not obtained due to sample decomposition; (d) 5: pmr (CCl₄): δ 6.75 (dd, 1H, J=9, 17), 5.01 (dd, 1H, J=2, 9), 4.99 (dd, 1H, J=2, 17), 3.44 (t, 2H, J=8), 1.1-2.5 (m, 8H), 0.85, 0.55 (AB, 2H, J=6); cmr (CDCl₃): 140.2, 112.7, 37.1, 35.1, 35.0, 31.8, 31.4, 30.7, 20.3, 18.7; ir (CCl₄): 3090, 1635 cm⁻¹. Anal. calcd for C₁₀H₁₅Br: m/e 214.0358; found: 214.0358.

7. 1: pmr (CCl₄): δ 4.55 (dd, 2H, J=4,6), 2.85, 1.85 (AB, 2H, J=9), 1.7-3.0 (m, 10H); cmr (CDCl₃): δ 154.9 (bridgehead C), 113.7, 41.2, 40.6, 37.4, 24.0; ir (CCl₄): 3040, 1650 cm⁻¹. Anal. calcd. for C₁₀H₁₄: m/e 134.1096; found: 134.1098.
8. See accompanying paper for force-field calculations which lead to this conclusion.
9. E. M. Kosower, W. J. Cole, G. S. Cardy, and G. Meisters, J. Org. Chem., 28, 630 (1963).
10. J. E. Starr and R. H. Eastman, ibid., 31, 1393 (1966).
11. 14: pmr (CCl₄): δ 5.8 (s, 1H), 3.78, 3.57 (AB, 2H, J=12), 2.5, 1.9 (AB, 2H, J=20), 1.2-2.9 (m, 8H); cmr (CDCl₃): δ 204.8, 173.9, 131.7, 54.0, 50.6, 49.6, 48.0, 36.0, 35.6, 16.5; ir (CDCl₃): 3070, 1715, 1622, 1225, 1210 cm⁻¹. Anal. calcd. for C₁₀H₁₃OCl: m/e 184.0655; found: 184.0647.
12. (a) H. O. House and T. V. Lee, J. Org. Chem., 44, 2819 (1979); (b) H. O. House, R. F. Sieloff, T. V. Lee, and M. B. De Tar, ibid., 45, 1800 (1980).
13. 15: pmr (CCl₄): δ 5.15 (s, 2H), 1.1-2.2 (m, 10H); ir (CCl₄): 3075, 3000, 1730, 1710, 1640, 1620 cm⁻¹; gcms: m/e 150 (P⁺); it is possible (cf. ir) that 15 was a mixture of 15 and bicyclo[4.3.1]deca-1,6-dien-8-one.

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