Tetrahedron Letters,Vol.28,No.42,pp 4965-4968,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

9,10-DIMETHYLENETRICYCLO[5.3.0.0^{2,8}]DECA-3,5-DIENE

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Summary: The title compound (3), a molecule whose central cyclobutane ring is 1,3-bonded in hybrid fashion to two butadiene units, has been prepared and its thermal stability assessed relative to 1 and 2.

The recently completed syntheses of 1[2] and 2[3] has permitted detailed analysis of the extent to which their central cyclobutane bonds can interact with mutually perpendicular π systems of different size.[4] Whereas 1 is intrinsically more capable of efficient relay conjugation than is spiro[4.4]nonatriene of through-space spiroconjugation,[5] 2 differs significantly. Only a minute (< 0.1%) $2a_2(\pi)$-$3a_2(\pi^*)$ interaction is seen by photoelectron spectroscopy.[6]


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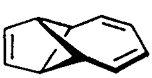

2


3

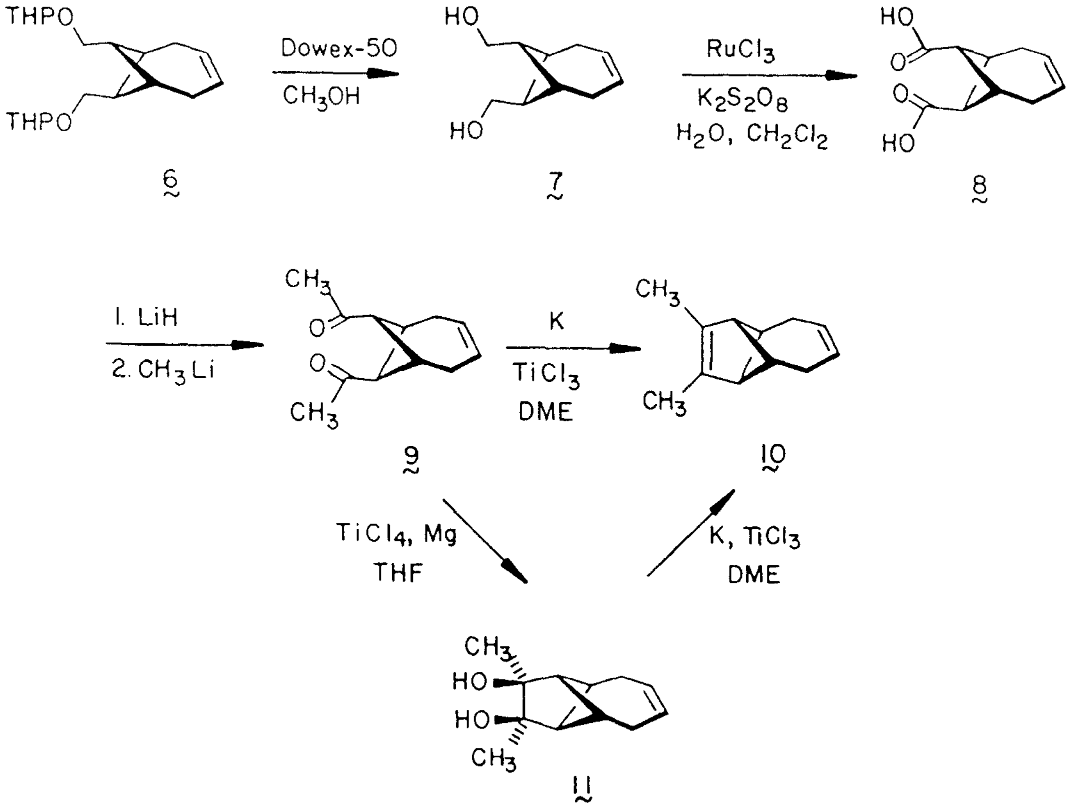

4


5

Other experimental investigations have shown 4 to undergo rapid isomerization to semibullvalene at room temperature,[7] and 5 to be capable of formation via a pyrolysis reaction at 380°C.[8] Differing electronic interactions between the π ribbons and the cyclobutane Walsh orbitals are suspected of being responsible for the widely divergent thermal stabilities.[9]

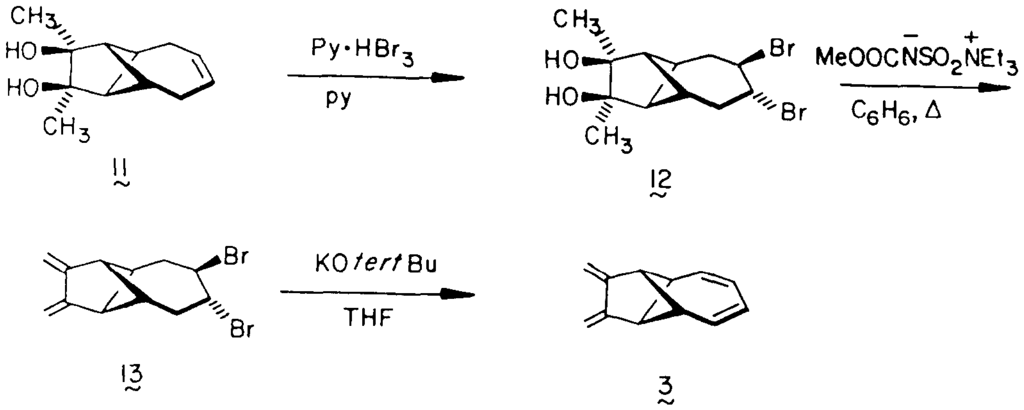
Herein we describe a synthesis of tetraene 3, the first cyclobutane to have hybrid connectivity to two butadiene units. Since the ethylene bridge in 2 at *ca* 1.34 Å is somewhat shorter than the central bond of butadiene (*ca* 1.48 Å),[9] the ring strain in 3 should be intermediate between that present in 1 and 2. On the other hand, the energy levels of the MO's of 3 resemble more closely those of 1 and the symmetries of the FMO's in both 1 and 3 are opposite to those present in 2.[4] Consequently, target compound 3 offers a unique opportunity to gain information on the relative importance of ring strain and electronic character in these systems.

The known diether 6[2] was initially deprotected by stirring with acid-washed Dowex-50 resin in methanol (91%)[10] and subsequently oxidized with high efficiency to diacid **8** (87%) using potassium ruthenate.[11] Following preparation of the dilithium salt of **8** by reaction with excess lithium hydride, addition of methyllithium[12] gave **9** (53%).

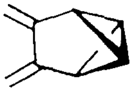


The first method examined for effecting the critical ring closure involved heating **9** with potassium metal and the $TiCl_3$•3THF complex in dimethoxyethane[13] with vigorous exclusion of oxygen and moisture. However, only 13% of impure diene could be isolated. Since neither the yield nor the purity of the hydrocarbon could be improved, recourse was made instead to pinacolic coupling as promoted by titanium tetrachloride and magnesium in THF.[14] These conditions led cleanly to diol 11 (76%) whose cis stereochemistry and resultant C_s symmetry are transparently obvious on the basis of its 9-line ^{13}C NMR spectrum. Submission of 11 to the McMurry deoxygenation conditions provided **10** in high purity, although again in undistinguished yield (18% based on recovered 11).

Consequently, diol 11 was instead brominated with pyridinium perbromide to give 12 (72%). When this polyfunctional molecule was heated in benzene with the Burgess reagent,[15] conversion to dibromide 13 took place (66% yield). Ultimate dehydrobromination of 13 with potassium *tert*-butoxide in tetrahydrofuran was achieved without complication



(86% isolated). The ^1H NMR spectrum of the resulting 3 exhibits the AA'BB'XX' pattern typical of cyclic 1,3-diene units and sharp singlets for the vinyl and bridgehead protons due to its 2,3-dimethylenebicyclo[2.1.1]hexane component, indicating the usual absence of spin-spin interaction there. Contraction of the flap angle of the cyclobutane ring by installation of a short bridge as in 14[16] or widening this same angle by the interposition of a 1,4-butadienyl ribbon as in 3 has little consequence on the chemical shift of the exo methylene protons. However, H_1 in 3 experiences a dramatic upfield shift to δ 1.75 in a manner paralleling the shielding encountered in related systems.[2,17]



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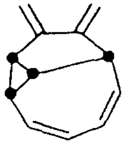

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When 3 was heated to 80°C in benzene solution, smooth first-order rearrangement occurred ($t_{\frac{1}{2}}$ = 65 min). The lone isomeric hydrocarbon produced was shown to be **15** by suitable C-H correlation and COSY studies at 500 MHz.[18] Thus, we see that 3 experiences formal 1,5-sigmatropic migration of a central cyclobutane bond across the flanking 1,4-bridged butadiene π-system. Comparison with the thermal responses of 1 and 2[2,3] is of interest and will be discussed elsewhere.

Photoelectron spectroscopic measurements to be made on 3 are expected to reflect the potentially unique electronic situation in this molecule.[19]

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(18) We thank Dr. C. E. Cottrell (Campus Chemical Instrumentation Center) for these measurements.

(19) The financial support of the National Science Foundation is gratefully acknowledged.

(Received in USA 1 July 1987)