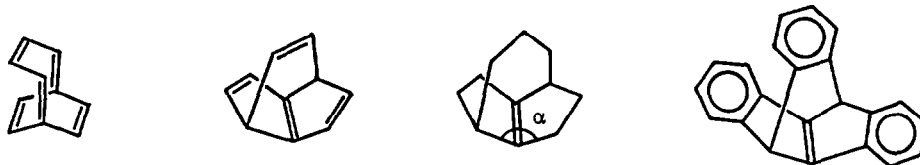


SYNTHESIS OF TRIBENZOTRICYCLO[5.3.0.0^{4,8}]DECA-2,5,7,9-TETRAENE:
A NEW STRAINED OLEFIN WITH HIGH UNSATURATION

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Summary: The title compound, the first derivative of highly strained and yet unknown tricyclo[5.3.0.0^{4,8}]deca-2,5,7,9-tetraene, was synthesized as a highly reactive olefin.

In the preceding paper, we described the synthesis of a tribenzo derivative of 5,6-dihydro compound of 1 which is a fully unsaturated bridgehead olefin with molecular formula of C₁₀H₈.¹⁾ Another novel and interesting C₁₀H₈ hydrocarbons having a strained double bond is tricyclo[5.3.0.0^{4,8}]deca-2,5,7,9-tetraene (2). As a related molecule, tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (3) has been reported to be a reactive substance.²⁾ While bridgehead olefins are strained mostly due to twist of double bond, the olefins 2 and 3 are strained due to out-of-plane deformation of the central double bond, and the dihedral angle α in 3 has been calculated to be 130° in contrast to the planar geometry ($\alpha = 180^\circ$) of the unbridged parent bicyclo[3.3.0]oct-1(5)-ene.³⁾ Because of the shorter bridge, 2 should be more deformed and accordingly a highly reactive substance. We wish here to report the first synthesis of a derivative of 2, the title compound 4.

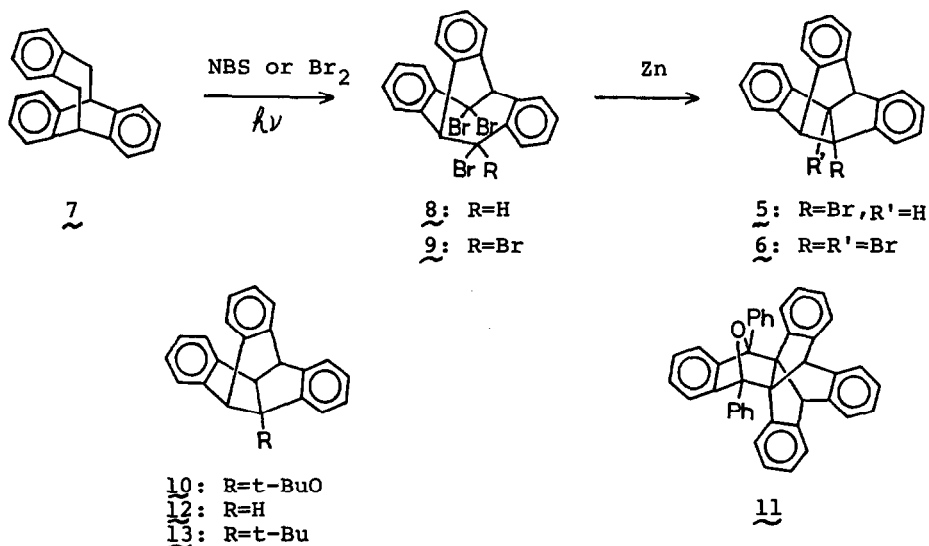


The suitable precursors for 4 would be the monobromide 5 or the dibromide 6. Cava et al. has briefly described the formation of 6, via the rearranged tetrabromide 9, upon bromination of 5,12[1',2']-benzenodibenzo[a,e]cyclooctene (7) with excess NBS followed by debromination with LiAlH₄ or zinc.⁵⁾ We could obtain 5⁶⁾ in moderate yield of 46% under a modified condition [i) 5.5 equivs of NBS, CCl₄, reflux, 20 h; ii) 5.0 equivs of Zn powder, DMF, 60 °C, 2 h]. The tetrabromination of 7 to 9 was found to be best accomplished by use of molecular bromine (7.0 equivs, 80% yield) under irradiation.

While the bromide 5 is inert to t-BuOK in a couple of solvents around room temperature, reaction of 5 with t-BuOK in boiling benzene in the presence of 18-crown-6 afforded the substitution product 10⁶⁾ in 83% yield. Because substitution by a S_N2 mechanism is impossible in 5, this result is best explained by dehydrobromination-addition mechanism, i.e. intermediacy of 4. Actually the

formation of 4 was proved by trapping as the Diels-Alder adduct 11 (79%)⁵⁾ when reaction with the base was carried out in the presence of 1,3-diphenylisobenzofuran. Similar dehydrobromination of 5 in the presence of 1,3-cyclohexadiene gave exclusively the reduction product 12⁶⁾ probably by hydride transfer from the diene to 4.⁷⁾

The olefin 4 could also be generated from the dibromide 6: treatment of 4 with excess *t*-BuLi in THF at -20 °C to room temperature afforded a mixture of two isomeric dimers of 4 (40%) in addition to the substitution product 13 (30%).⁶⁾ Similar dimers were also obtained by debromination with Na-K alloy in benzene. The dimers lack symmetry as judged by ¹H and ¹³C NMR spectra, and further studies in regard to the structures are in progress.



References and Notes

- 1) M. Toda, K. Okada, and M. Oda, the preceding paper.
- 2) R. Greenhouse, W. T. Borden, T. Ravindranathan, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, **99**, 6955 (1977).
- 3) F. M. Wilhelm and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 1891 (1981).
- 4) M. P. Cava, M. Krieger, R. Pohlke, and D. Mangold, *J. Am. Chem. Soc.*, **88**, 2615 (1966).
- 5) 5: mp 199-200 °C; ¹H NMR (100 MHz, CDCl₃), δ 4.15 (1H, d, J=6.2 Hz), 4.37 (1H, d, J=1.0 Hz), 4.56 (1H, dd, J=6.2, 1.0 Hz), 6.91 (4H, s), 7.02-7.60 (8H, m).
10: mp 218-219 °C; ¹H NMR (100 MHz, CDCl₃), δ 1.06 (9H, s), 3.91 (1H, d, J=1.5 Hz), 4.22 (1H, d, 5.2 Hz), 4.67 (1H, dd, J=5.2, 1.5 Hz), 6.89 (4H, s), 6.99-7.48 (8H, m).
11: mp 272-273 °C; Mass, m/z 548 (M⁺, 100%), 278 (24), 270 (34); ¹H NMR (90 MHz, DCD₁₃), δ 4.19 (1H, s), 4.72 (1H, s), 5.88 (1H, s), 6.48-7.88 (24H, m), 8.11 (1H, d, J=7.2 Hz).
13: oil; ¹H NMR (CDCl₃, 90 MHz), δ 0.99 (9H, s), 4.02 (1H, d, J=4.8 Hz), 4.14 (1H, s), 4.17 (1H, d, J=4.8 Hz), 6.78-7.51 (12H, m).
- 6) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **28**, 1012 (1963).
- 7) J. E. Hofmann, P. A. Argabright and A. Schriesheim, *Tetrahedron Lett.*, 1005 (1964).

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