Tetrahedron Letters No. 7, pp 667 - 670, 1978. Pergamon Press. Printed in Great Britain.

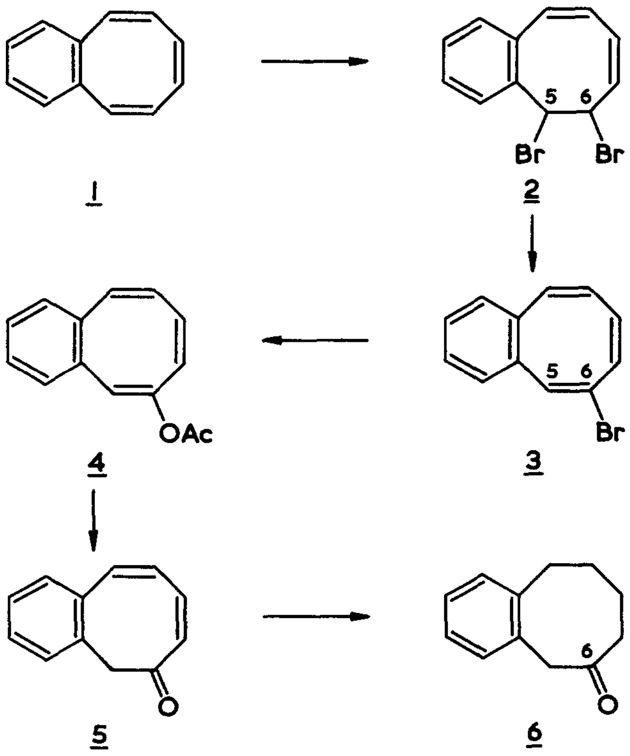
CYCLIC CONJUGATED CUMULENES. 6,7-DIDEHYDROBENZOCYCLOOCTENE[1]

Henry N.C. Wong, Tze-Lock Chan and Franz Sondheimer*
Chemistry Department, University College
20 Gordon Street, London WC1H OAJ

(Received in UK 12 December 1977; accepted for publication 28 December 1977)

Hitherto, no completely conjugated medium-size cyclic cumulene has been known.[2] We now report the formation of the title compound, the first example of this type of substance, as a transient intermediate.[3]

Treatment of benzocyclooctene (1)[4] with 1 molar equivalent of bromine in methylene chloride at -70 °C yielded 40 % of the known[4] 5,6-dibromide (2), m.p. 67 - 70 °C. Dehydrobromination of 2 with *ca* 1.3 molar equivalents of potassium *t*-butoxide in dry tetrahydrofuran at room temperature for 1 hour led to the yellow liquid 6-bromobenzocyclo-



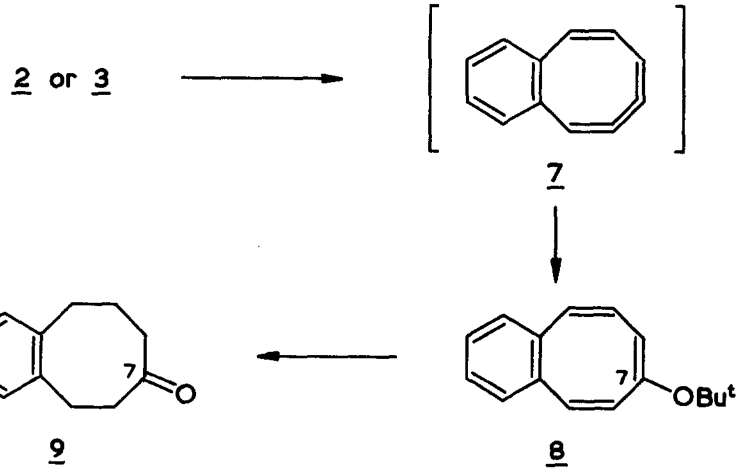
octene (3)[5a,6]: MS *m/e* 231.9892 (M^+, calcd 231.9888); UV (hexane) λ_{max} 244 nm (ε 15,600). The ^{1}H NMR spectrum was complex, and did not allow a distinction between the 5- and 6-bromo structures to be made. It was found best to carry out the dehydrobromination of crude (2), whereby (3) was obtained in 66 % over-all yield (based on (1)).

Treatment of the 6-bromide (3) with freshly prepared silver acetate (1.1 molar equivalents) in glacial acetic acid[7] at 100 °C for 22 hours led to the crude acetate (4), which was hydrolyzed directly with 60 % aqueous sulphuric acid in boiling tetrahydrofuran for 30 minutes. Isolation[5b] then yielded 63 % (based on (3)) of 5,6-dihydrobenzocycloocten-6-one (5) as a yellow oil:[6] MS *m/e* 170 (M^+, calcd 170); ^{1}H NMR (60 MHz, $CDCl_3$) τ 2.65 (m, 4H, aryl H), 2.85 - 3.75 (m, 4H, olefinic H), 6.38 (s, 2H, CH_2); UV (cyclohexane) λ_{max} 223 nm (ε 20,800), 256 sh (16,400), 288 (5,100); IR (film) 1670 cm^{-1} (s) ($\alpha\beta$-unsatd. C=O). Substance (5) was further characterized as the 2,4-dinitrophenylhydrazone,[6] crimson needles, m.p. 176 - 178 °C. Other methods for converting (3) to (5) were employed, but proved to be less satisfactory.

Catalytic hydrogenation of the unsaturated ketone (5) in ethyl acetate over 10 % palladium-charcoal gave 90 % of 5,6,7,8,9,10-hexahydrobenzocycloocten-6-one (6) as a colourless oil, which was characterized as the known oxime,[6] m.p. 130 - 131 °C (lit.[8] m.p. 129.5 - 130 °C). The carbon skeleton of (6) was confirmed by Wolff-Kishner reduction to 5,6,7,8,9,10-hexahydrobenzocyclooctene.

Treatment of the dibromide (2) with a larger excess of potassium *t*-butoxide (*ca* 10 molar equivalents) in dry tetrahydrofuran at room temperature for 1 hour led to only 19 % of the 6-monobromide (3), and mainly (67 %) to 7-*t*-butoxybenzocyclooctene (8), a pale yellow oil:[9] MS *m/e* 226.1347 (M^+, calcd 226.1358); ^{1}H NMR (60 MHz, $CDCl_3$) τ 2.60 - 3.10 (m, 4H, aryl H), 3.20 - 4.08 (m, 5H, olefinic H), 8.64 (s, 9H, *t*-Bu); UV (cyclohexane) λ_{max} 240 nm (ε 11,900). Similarly, treatment of the 6-monobromide (3) with *ca* 5 molar equivalents of potassium *t*-butoxide yielded 43 % of the 7-*t*-butoxy compound (8), as well as 42 % of unchanged (3).

The structure of the 7-*t*-butoxy compound (8) was confirmed through catalytic hydrogenation of the 5,6- and 9,10-double bonds in ethyl acetate over 10 % palladium-charcoal. Hydrolysis of the resulting enol ether in dioxane with concentrated sulphuric acid for 15 minutes at room temperature led to 26 % (based on (8)) of 5,6,7,8,9,10-



hexahydrobenzocyclooctene-7-one (9)[9], m.p. 49 - 51 °C (lit.[10] m.p. 48.5 - 50.5 °C); the oxime showed m.p. 108 - 110 °C (lit.[10] m.p. 112.5 - 114 °C).

There is little doubt that the conversion of the bromides (2) and (3) to the *t*-butoxy compound (8) involves the cyclic conjugated eight-membered cumulene (7) as a transient intermediate. Unfortunately, this cumulene proved to be too unstable for isolation or independent trapping (*e.g.*, with 1,3-diphenylisobenzofuran) to be possible, and no physical data could be obtained.

Acknowledgements. Awards of a Shell Postgraduate Scholarship (administered by the Chinese University of Hong Kong) to H.N.C.W., and a Commonwealth Academic Staff Fellowship to T.L.C., are gratefully acknowledged.

References and Notes

1. Unsaturated Eight-Membered Ring Compounds. XIV. For Part XIII, see H.N.C. Wong, F. Sondheimer, R. Goodin, and R. Breslow, *Tetrahedron Lett.*, 2715 (1976).
2. Examples of non-conjugated cyclic cumulenes: 1,2,3-cyclodecatriene (W.R. Moore and T.M. Ozretich, *Tetrahedron Lett.*, 3205 (1967)); 1,4,7,10-tetraphenyl-1,2,3,7,8,9-cyclododecahexaene [W. Jasiobedski, *Roczniki Chem.*, **41**, 1265 (1967); *Chem. Abst.*, **68**, 29,344e (1968)]; 3,4,5,10,11,12-cyclotetradecahexaene-1,8-dione (P.J. Garratt

K.C. Nicolaou, and F. Sondheimer, *J. Org. Chem.*, **38**, 2715 (1973)). For examples of conjugated macrocyclic acetylene-cumulenes, see M. Nakagawa in "Topics in Nonbenzenoid Aromatic Chemistry", Ed. T. Nozoe, R. Breslow, K. Hafner, Shô Itô and I. Murata, Hirokawa Publishing Co. Inc., Tokyo, Vol I, 1973; *Pure and Applied Chem.*, **44**, 885 (1975).

3. The unstable intermediate obtained by the dehydrobromination of bromocyclooctatetraene with potassium *t*-butoxide might also be a conjugated cyclic cumulene, but no evidence for this formulation was obtained (A. Krebs, *Angew. Chem.*, **77**, 966 (1965); A. Krebs and D. Byrd, *Justus Liebigs Ann. Chem.*, **707**, 66 (1967)).
4. *Inter al*, see J.A. Elix and M.V. Sargent, *J. Am. Chem. Soc.*, **91**, 4734 (1969).
5. The substance was isolated by chromatography on (a) silica gel; (b) alumina.
6. A satisfactory elemental analysis was obtained.
7. Method of J. Gasteiger, G.E. Gream, R. Huisgen, W.E. Konz, and U. Schnegg, *Chem. Ber.*, **104**, 2412 (1971).
8. R. Huisgen, E. Rauenbusch, and G. Seidl, *Chem. Ber.*, **90**, 1958 (1957).
9. Separated by plc on Merck Kieselgel 60 PF_{254}.
10. E.M. Fry and L.F. Fieser, *J. Am. Chem. Soc.*, **62**, 3489 (1940).