Tetrahedron Letters No.51, pp. 4475-4478, 1969. Pergamon Press. Printed in Great Britain.

IMPROVED SYNTHESES OF 1,6-BRIDGED-[10]ANNULENES[1]

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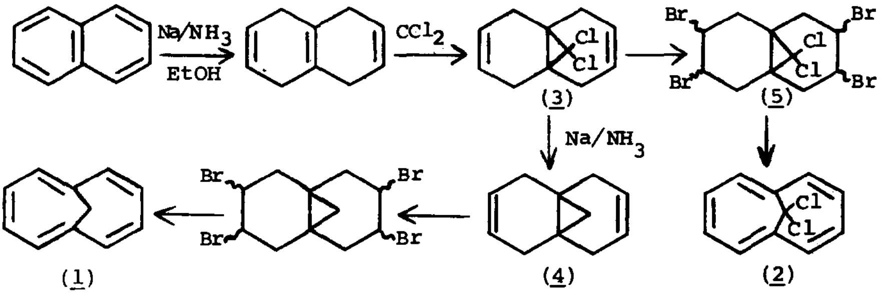
(Received in USA 12 September 1969; received in UK for publication 3 October 1969)

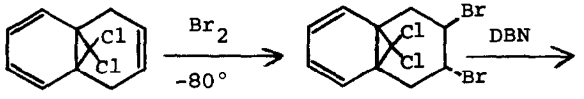
The interesting bridged cyclodecapentaenes, 1,6-methano-[10]annulene (1) and the 11,11-dichloro-analogue (2), were first synthesized by Vogel, et al[2,3] by the routes shown in Scheme I.

SCHEME I



The yield of (1) by this method is good [(4) $\longrightarrow$ (1) ca. 50% overall] but that of the dichloro compound (2) is less satisfactory (dehydrobromination of (5) to (2) proceeded in only 6% yield).[3]

We have found that the yields of both of these annulenes can be greatly increased by the use of dichlorodicyanobenzoquinone (DDQ) for the oxidation of the dienes (3) and (4). When (4) is refluxed with 2.5 moles DDQ in dioxan for 1/2 to 2 hrs., (1) is produced in 90% yield.[4] Similar treatment of (3) produced the norcaradiene compound (6)[5] (70%) which was not oxidized further by DDQ in refluxing dioxan even in the presence of a trace of p-toluenesulfonic acid. DDQ in refluxing diglyme (160°) did consume (6) and, after 50% reaction, naphthalene was produced (ca. 35%), which could have arisen from thermal decomposition of (2).[3] However, (6) could be converted into (2) in 75% overall yield *via* the dibromide (7)[6] which gave (2)[7] on treatment with diazabicyclononene (dimethylformamide, 48 hrs., 25°).[8] The overall conversion of (3) to (2) is thus approximately 50%.



(6) (7) (2)

Having found this very facile oxidation of the diene (4) to (1), we investigated the possibility of adding a methylene group preferentially to the tetrasubstituted double bond of isotetralin. This was accomplished by a modified Simmons-Smith reaction.[9] Treatment of isotetralin (20.0 g) with a reagent prepared from cuprous chloride (30.0 g), zinc (66.0 g) and methylene iodide (60 ml) gave (4) in *ca.* 50% yield.[10] Thus, 1,6-methano-[10]annulene can be prepared from naphthalene in *ca.* 40% overall yield in a three-step process.

The oxidations of (4) to (1) and (3) to (6) can be carried out using chloranil or 1,4-benzoquinone, but these reactions are slower than those using DDQ.

The oxidation of an unactivated disubstituted olefin to a diene has wide synthetic applications, some of which are at present under investigation. A related oxidation of tetramethylethylene to 2,3-dimethylbutadiene[11] was recently reported.[12]

Acknowledgment

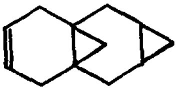
We thank Mr. G. Bartsch for performing the chloranil and benzoquinone oxidations.

REFERENCES

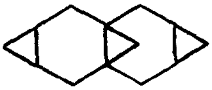
1. Contribution No. 362 from the Syntex Institute of Organic Chemistry; for No. 361 see A. T. Christensen, Acta Cryst., in the press.
2. E. Vogel and H. D. Roth, Angew. Chem. 76, 145 (1964); Angew. Chem. Internat. Edit., 3, 228 (1964).
3. V. Rautenstrauch, H.-J. Scholl and E. Vogel, Angew. Chem. Internat. Edit., 7, 288 (1968).
4. At the conclusion of the reflux period, the solution is cooled and added to *ca*. 5 volumes of hexane. The solution is filtered, washed several times with water, dried and passed through a short silica gel column. The eluate upon evaporation gives (1) identical in all respects to a sample produced by the Vogel synthesis.
5. m.p. 125-126°; λ_{max} 278 mμ (ε 1600); nmr (100 MHz) 2.15, 2.32, 2.79, 2.97 (AB pattern, J_{AB} 17 Hz, $-CH_2$), 5.51 (olefinic H), 5.7-5.9, 6.1-6.3 ppm (A_2B_2 pattern, diene-H), M.S. 212 (M^+). Anal. Calcd. for $C_{11}H_{10}Cl_2$: C, 62.00; H, 4.70; Cl, 33.31. Found: C, 62.39; H, 4.79; Cl, 33.65.
6. m.p. 99-101°; λ_{max} 279 mμ (ε 1900).
7. The melting point of this compound varies with the rate of heating. Consistent readings within the range 116-120° are obtainable with relatively rapid heating. In all cases the crystals became opaque at *ca*. 90°. Vogel *et al* report m.p. 104-107° (dec.). The mass spectrum of (2) exhibits absorptions at m/e 210, 212 and 214 and m-1/e 209, 211, 213 (m-1/e 3x m/e).
8. (7) was unaffected by potassium hydroxide in refluxing methanol.
9. Drs. R. J. Rawson and I. T. Harrison in these laboratories have developed simplified *in situ* procedures for olefin-to-cyclopropane conversions. A full account of their work will be published shortly. The procedure used here was to stir at reflux a mixture of cuprous chloride, zinc dust and diethyl ether for 30 min., add methylene iodide, and reflux for a further 30 min. The olefin was then added and the mixture was stirred at room

temperature for 16 hrs.

10. GLC analysis of a typical reaction showed: (4) 50%; isotetralin (5%); bis-adducts (8) (27%) and tris-adducts (9) (12%). (4) is isolated by fractional distillation of this mixture.



(8)



(9)

11. Isolated as the Diels-Alder adduct with DDQ.

12. A. E. Asato and E. F. Kiefer, Chem. Commun. 1684, 1968.