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OLEFINIC AND ACETYLENIC COMPOUNDS—II*

NEW ROUTES TO DIBENZOBARRELENES

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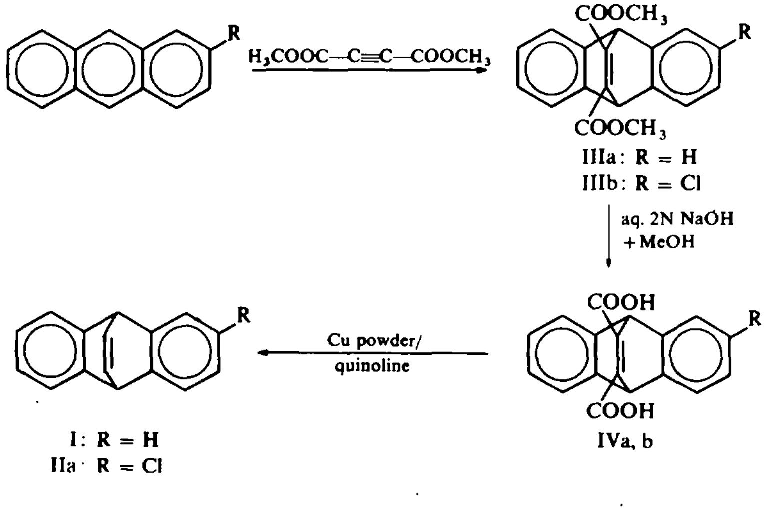
Abstract—Two new high-yield syntheses of dibenzobarrelene have been developed and applied to the case of 2-substituted derivatives; 2-chloro- and 2-cyanodibenzobarrelene have been synthesized.

DIBENZOBARRELENE (I) (9,10-dihydro-9,10-ethenoanthracene) has been synthesized in recent years by several authors, either in very poor yields[1,2] or by using high-pressure and high-temperature procedures.[3] The most convenient laboratory method has been developed by Cristol *et al.*,[4] who synthesized (I) by the Diels–Alder addition of *cis*- or *trans*-dichloro-ethylene on anthracene followed by a dechlorination reaction using sodium in refluxing n-pentanol or isopropanol.

The purpose of this work was to find new routes leading to dibenzobarrelenes substituted in position2. Indeed, when Cristol's method was applied to 2-substituted anthracenes, the dechlorination conditions proved to be too drastic for most of them.

SCHEME A



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[*] Part I, H. P. Figeys and M. Gelbcke, *Tetrahedron Letters*, 5139 (1970).

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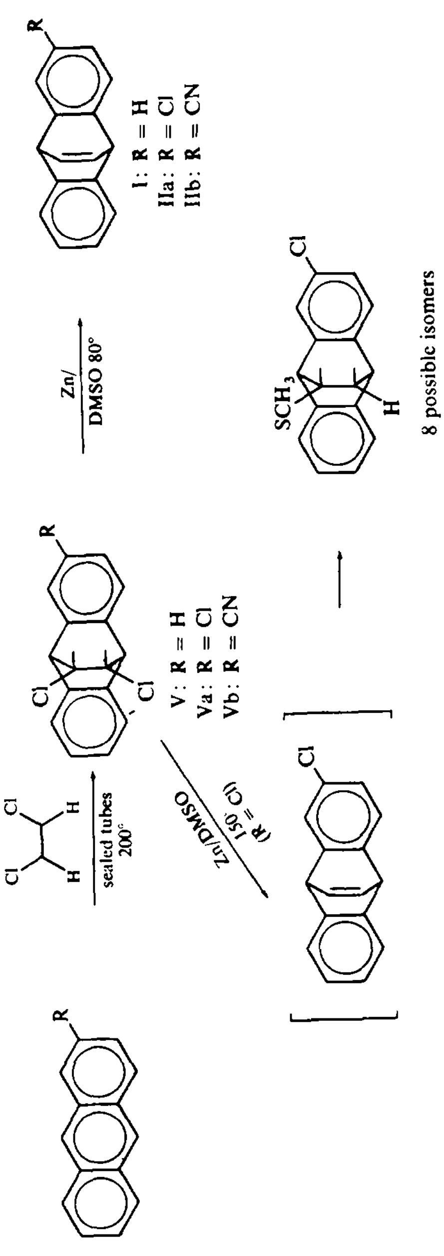
SCHEME B


R
sealed tubes
200°
Cl
H
V : R = H
Va : R = Cl
Vb : R = CN
Zn/
DMSO 80°
I : R = H
IIa : R = Cl
IIb : R = CN
Zn/DMSO
150° Cl)
(R =
SCH$_3$
8 possible isomers

For example, with either the nitrile or the ester group, only inseparable mixtures showing strong absorption in the aliphatic region of the 1H-NMR spectrum were isolated; furthermore, aromatic Cl 11,12-*cis*-dichloro-9,10-dihydro-9,10-ethanoanthracene (Va) gives I in nearly quantitative yield.

We wish to report here two high-yield syntheses of dibenzobarrelene and of the 2-chloro and 2-cyano derivatives (IIa and IIb).* In the course of this work, a new synthesis of 2-cyanoanthracene has also been worked up.

The addition of dimethylacetylene carboxylate to anthracene or to 2-chloroanthracene gives respectively 9,10-dihydro-9,10-(1'2'-dicarbomethoxy)-ethenoanthracene (IIIa)[6] or the corresponding chloro derivative (IIIb) in fair yield (90% and 60% respectively); these can be converted readily into the corresponding diacids (IVa, b) which are then decarboxylated using copper powder in refluxing quinoline to give respectively dibenzobarrelene (I) and 2-chlorodibenzobarrelene (IIa). The overall yield obtained for I is 71%.†

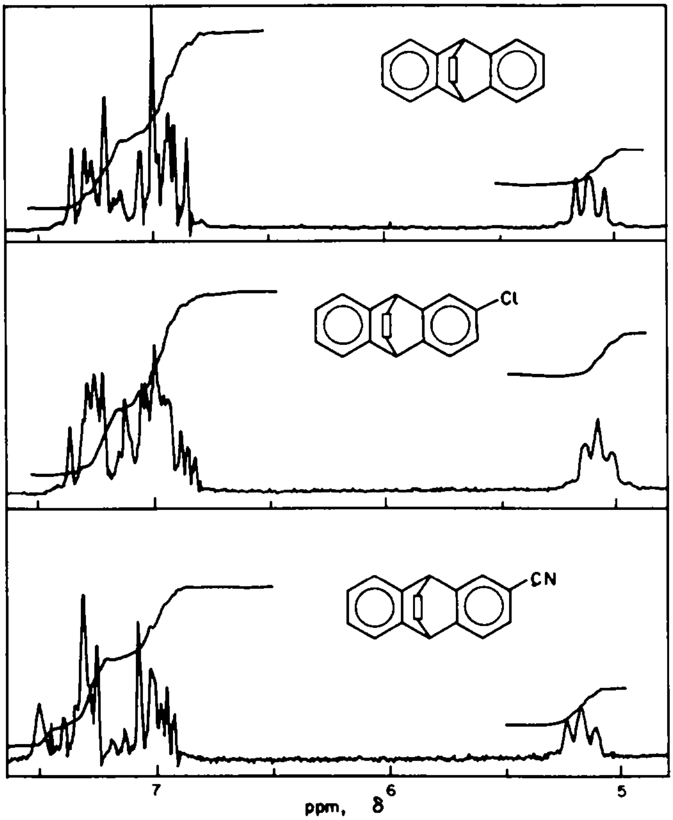


FIG 1. 60 MHz spectra of dibenzobarrelene and the 2-chloro and 2-cyano derivatives (see text)

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* To our knowledge, the only reported dibenzobarrelene substituted in one of the benzene rings is the 2-chloro derivative described by Friedman *et al.*[5] The reaction scheme used by these authors is not described.

† In our hands, the yield obtained by Cristol's method starting with *cis*-dichloroethylene, is 56% (purified product).

The other obvious way to the desired products is to find smoother conditions for the dechlorination of derivatives (Va, b) in order to avoid the loss of chlorine and other side reactions.

Attempts to realise this dechlorination by sodium iodide in different solvants (acetone, DMF, DMSO, or 2,2-ethoxy-ethoxy-ethanol) failed. However, Cristol *et al.*[4a] showed that V is converted into I by zinc dust in ethanol in 43% yield after 12 days. Recently, Montijn *et al.*[7] found that the dechlorination of 1,4-dichloro-2-butyne to give butatriene, which is very slow in ethanol, is strongly accelerated by the use of "aprotic dipolar solvents" such as DMF, DMSO, or sulfolane.

The same is true in the case of V and Va which are converted by zinc dust in DMSO at 80° to I and IIa in almost quantitative yield after 7 and 12 days respectively; compound Vb is converted to IIb after 10 days in 65% yield. The reaction is followed by Volhard's titration method.[8]

In the case of the 2-chloro derivative, an attempt was made to decrease the reaction time by increasing the temperature; after 6 days at 150° a colourless oil is obtained in quantitative yield. The same oil is also obtained by warming 2-chlorodibenzobarrelene in DMSO at 150° in the presence of zinc dust. Elemental analysis, M.S. (M^+ $m/e = 286$), and NMR spectroscopy showed that this product results from the addition of methyl mercaptan (formed by the decomposition of the solvent) on the C═C double bond of 2-chlorodibenzobarrelene:

EXPERIMENTAL

The dibenzobarrelene derivatives were identified by the usual spectroscopic methods. The NMR spectra of the three compounds described in this paper are shown in Fig 1 (Varian A 60-MHz instrument; CDCl$_3$ solutions: 10% w:v; TMS = 0). The aromatic and olefinic protons form a complex pattern extending from 405 to 450 Hz: the bridge-head protons appear as a symetrical multiplet (part A of a AA'XX' system) centred at 308 Hz for (I), 305 Hz for (IIa), and 311 Hz for (IIb). UV spectra, measured with a Beckman DB-GT spectrophotometer, refer to solns in cyclohexane; IR spectra were measured for potassium bromide disks with a Perkin-Elmer model 237 instrument and only the strongest bands are reported; mass spectra were recorded with an Hitachi RMU-6D spectrometer at 70 eV.

Scheme A

9,10-dihydro-9,10-(1',2'-dicarbomethoxy)-ethenoanthracene (IIIa) *and the corresponding 2-chloro derivative* (IIIb). These products were obtained by the addition of acetylene dimethylcarboxylate to anthracene or 2-chloroanthracene[9] by the procedure described.[6] After recrystallization from MeOH; IIIa (m.p. 160–1°; lit.[6] m.p. 160–1°) and IIIb (m.p. 138°) were obtained in 90% (lit.[6] 100%) and 60% respectively.

Corresponding diacids (IVa, b). The two diesters (IIIa, b) were quantitatively converted into the corresponding diacids by refluxing in a mixture of MeOH and 2N NaOH (40:60) for 1 hr (IVa: m.p. 215·5–216°; IVb: m.p. 198°).

Dibenzobarrelene (I) *and 2-chlorodibenzobarrelene* (IIa). The diacid (500 mg) was refluxed in quinoline (1 ml) in the presence of Cu powder (86 mg). The reflux was maintained for 15 min after the evolution of gas had ceased. After cooling, the solution was diluted with chloroform (10 ml) and filtered; the Cu powder was extensively washed with chloroform, and the combined fractions successively washed with 10% NaOHaq, water, 10% HClaq, and again with water. The organic layer was dried and evaporated under reduced pressure. The residue was chromatographed on silica gel (50 g, 30–50 mesh, Merck A.G.; light petroleum b.p. 60–70°). The first eluated compound was a trace of the anthracenic derivative which resulted from the retro-Diels–Alder reaction, followed by the dibenzobarrelene derivative.

Dibenzobarrelene (m.p. 119°, lit.[4b] m.p. 119–120·5°) was obtained in 79% yield and identified by comparison with an authentic sample synthesized by Cristol's method; λ_{max} 280, 273, and 216·5 nm (log ε 3·43, 3·34, and 3·32): ν_{max} 1470, 750, and 690 cm^{-1}; mass spectrum M^+ m/e 204.

2-Chlorodibenzobarrelene (IIa) (m.p. 123°, lit.[5] m.p. 123–124·5°) was obtained in 37% yield (Found: C, 80·4; H, 4·6; Cl, 14·9. Calc. for $C_{16}H_{11}Cl$: C, 80·5; H, 4·6; Cl, 14·9%); λ_{max} 286, 280, and 219 nm (log ε 3·43, 1·38, and 4·44); ν_{max} 1460, 760, and 695 cm^{-1}; mass spectrum M^+ *m/e* 238.

Scheme B

2-*Chloro*-11,12-cis-*dichloro*-9,10-*dihydro*-9,10-*ethanoanthracene* (Va). 2-Chloroanthracene (4 g; m.p. 223°)[9] and *cis*-dichloroethylene (40 ml) were heated at 200° for 60 hr in a sealed tube of 55 ml. The excess dichloroethylene was recovered by distillation and the resulting black oil adsorbed on alumina and chromatographed (200 g of standard alumina); elution with light petroleum (b.p. 60–70°) gave first the unreacted 2-chloroanthracene and then Va. Conversion: 64%. The crude product was recrystallized from CCl_4 as white granules, m.p. 165–6°; yield: 83% (Found: C, 61·8; H, 3·4; Cl, 34·4. Calc. for $C_{16}H_{11}Cl_3$: C, 62·0; H, 3·6; Cl, 34·4%).

2-*Cyano*-11,12-*dichloro*-9,10-*dihydro*-9,10-*ethanoanthracene* (Vb). This product was obtained by the same method, starting with 2-cyanoanthracene and with *cis*- or *trans*-dichloroethylene; *cis* derivative: m.p. 183–5°; yield: 85%; (Found: C, 67·9; H, 3·8; Cl, 23·8; N, 4·5. Calc. for $C_{17}H_{11}Cl_2N$: C, 68·0; H, 3·7; 23·6; N, 4·7%); *trans* derivative: m.p. 140–1°; yield 96%.

2-*Chlorodibenzobarrelene* (IIa). Compound Va (9 g) and activated Zn dust (180 g) in DMSO (750 ml) (DMSO: dried over molecular sieves) was heated with stirring at 80° for 12 days. After filtration on celite, the DMSO was removed under reduced pressure and the residue diluted with chloroform, washed with water, 10% HCl aq, and again with water. After drying, the chloroform was evaporated under reduced pressure; 7 g of crude 2-chlorodibenzobarrelene were collected and recrystallized from EtOH in the presence of Norit; yield: 92%; m.p. 123°.

2-*Cyanodibenzobarrelene* (IIb). This product (m.p. 171°) was obtained from the *trans* derivative of Vb in 65% yield after 10 days: λ_{max} 290, 282, 260, and 226 nm (log ε 3·40, 3·40, 3·60, and 4·87); ν_{max} 2220 (C≡N), 1455, 1320, 810, 750, and 690 cm^{-1}; mass spectrum M^+ *m/e* 229; (Found: C, 88·4; H, 4·7; N, 6·0. Calc. for $C_{17}H_{11}N$: C, 89·1; H, 4·8; N, 6·1%).

Dibenzobarrelene (I). The unsubstituted derivative itself was obtained from V after 7 days in 92% yield.

2-*Cyanoanthracene*.[10] 2-Cyanoanthraquinone was obtained from 2-bromoanthraquinone[11] by the method of Friedman and Schechter:[12] yield: 93%; m.p. 217° (lit.[13] m.p. 216–7°). This product was then reduced (Zn in NH_4OH) to 2-cyanoanthracene by the procedure of Fisher and Ziegler:[9] yield: 81%; m.p. 200° (lit.[14] m.p. 199–200°).

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