254. Synthesis of Cycloprop[*b*]anthracenes *via* Trapping of *o*-Naphthoquinodimethane

by **Paul Müller*** and **Domingo Rodriguez**

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

(5.X.1983)

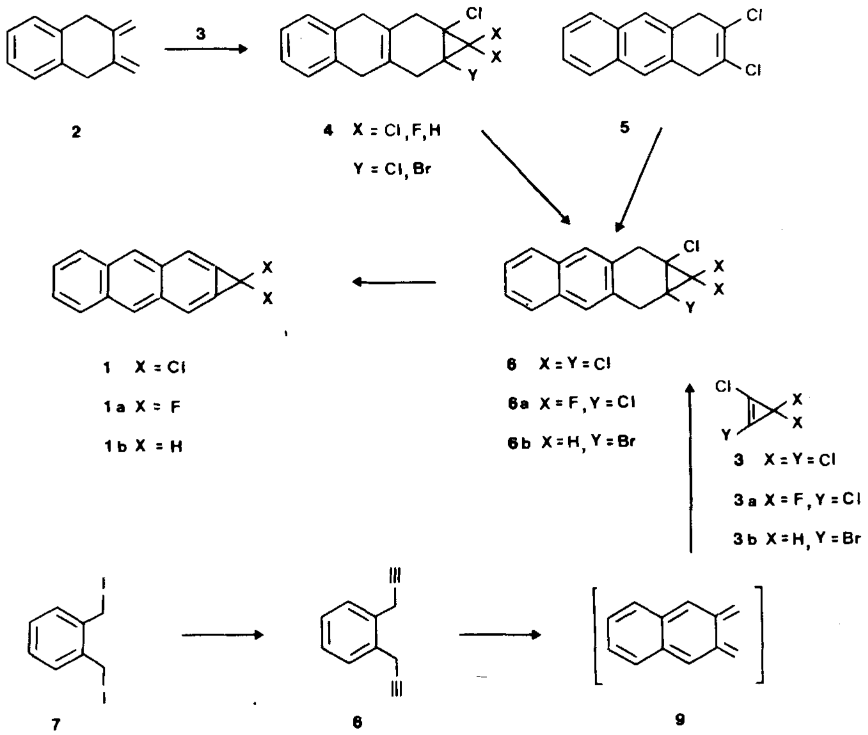
Summary

Cycloprop[*b*]anthracenes **1**, **1a**, **1b** are prepared in a 3-step synthesis starting from *o*-di(iodomethyl)benzene. The key step consists of trapping of *o*-naphthoquinodimethane (**9**) with 1,2-di- and tetrahalogenocyclopropenes (**3**, **3a**, **4b**).

In previous communications we have reported the synthesis of 1,1-dihalogenocycloprop[*b*]anthracenes **1** and **1a** [1]. The key step involved cycloaddition of 2,3-dimethylidene-1,2,3,4-tetrahydronaphthalene (**2**) to tetrahalogenocyclopropene **3**. The cycloadduct **4** was first dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to **5** and subsequently aromatized by treatment with *t*-BuOK. Several approaches were directed towards preparation of the parent compound, cycloprop[*b*]anthracene (**1b**), for example *via* reduction of **1** with $LiAlH_4/AlCl_3$ [2] or cyclopropanation of suitably 2,3-disubstituted-1,4-dihydroanthracenes **5**, but none were successful. A new scheme was then developed based on the trapping of *o*-quinodimethanes with cyclopropenes. The only precedent for this approach is the electrocyclic ring opening of *trans*-1,2-diphenylbenzocyclobutene followed by addition to tetrachlorocyclopropene which was used in the synthesis of 1,1-dichloro-2,7-diphenylcyclopropa[*b*]naphthalene [3]. However, the reaction is not general; in particular it fails with unsubstituted benzocyclobutene, mainly because of the decomposition of tetrachlorocyclopropene at the temperature required for benzocyclobutene ring opening.

Since we considered 1,2-dihalogenocyclopropenes potentially explosive [4] it appeared necessary to generate the *o*-quinodimethane at low temperature. An elegant method for this has been used by *Sondheimer et al.* [5] and worked out in all details by *Roth & Bartmann* [6]. *o*-Di(iodomethyl)benzene (**7**) is converted to *o*-di(2-propynyl)benzene (**8**) [6]. Upon treatment with *t*-BuOK in THF/*t*-BuOH **8** isomerized to the *bis*-allene at –78°. The latter is extracted with hexane. It cyclizes upon standing to *o*-naphthoquinodimethane (**9**) at *ca.* 30°. The latter can be trapped by addition of dienophiles to the cooled solution, which is allowed to warm up to 25°. *Roth & Bartmann* [6] obtained yields of 90–100% for trapping with *trans*-1,2-dichloroethene, O_2 and SO_2. The reaction of **8** with O_2 has also been reported by *Gisin & Wirz* [7].

Scheme



When **9** was generated in the presence of tetrahalogenocyclopropenes **3** or **3a** the corresponding cycloadducts **6** and **6a** were formed in moderate yield *(Table)*. The compounds were identical to those prepared previously in our laboratory by the route starting from **2** [1]. Treatment with *t*-BuOK afforded the previously described 1,1-dichloro- and 1,1-difluorocycloprop[*b*]anthracenes **1** and **1a**. The low yields for trapping are probably due to the low excess of cyclopropene used, but so far no attempt has been made to improve this step of the sequence. Despite this drawback, the new approach towards cycloprop[*b*]anthracenes is superior to the previous one, since it requires only 4 steps, starting from cheap, commercial material. In comparison, the preparation of **2**, which had been used in the first synthesis, requires *ca.* 8 steps alone [1] [8].

Table. *Trapping of 9 with Cyclopropenes*[a])

Dienophile	Excess	Adduct	Yield
3	5:1	**6**	23%
3a	4:1	**6a**	18%
3b	1:1	**6b**	40%

[a]) Conditions according to [6], 5–10 mmol scale.

While this work was in progress we were informed by *Billups et al.* [9] that a newly developed synthon, 1-chloro-2-bromocyclopropene (**3b**) undergoes smooth cycloaddition to **2**. Aromatization of the adduct, first with DDQ, then with *t*-BuOK afforded cycloprop[*b*]anthracene (**1b**). The successful synthesis of **1b** terminates speculations that it might not be capable of existence because of bond fixation [10].

We have repeated the preparation of **3b** according to *Billups et al.* [9] and confirmed its structure by reaction with diphenylisobenzofuran. Compound **3b** reacted with **9** to form the adduct **6b**, the structure of which was verified by comparison of the spectral data with those reported by *Billups*. Additional structural proof was obtained by dehydrohalogenation of **6b** to **1b** with *t*-BuOK under the usual conditions [1] [9].

Experiments involving the trapping of *o*-benzoquinodimethane, prepared by several procedures [5] [11] have so far given no positive results.

Financial support by the *Swiss National Science Foundation* (Project No. 2.236-0.81) is gratefully acknowledged. One of the authors *(D.R.)* thanks the sponsors of the '*Bourse Givaudan*' for a scholarship. We are indebted to Prof. *W.R. Roth*, University of Bochum, for the detailed experimental procedure for preparation of **9** and to Prof. *E. Billups* for sending us a preprint of his article for synthesis of **1b**.

REFERENCES

[1] *P. Müller & M. Rey*, Helv. Chim. Acta *65*, 1157 (1982); *64*, 354 (1981).

[2] *P. Müller*, Helv. Chim. Acta *57*, 704 (1974).

[3] *A.R. Browne & B. Halton*, J. Chem. Soc., Chem. Cummun. *1972*, 1341.

[4] *R. Breslow, G. Ryan & J.T. Groves*, J. Am. Chem. Soc. *92*, 988 (1970).

[5] *D.A. Ben-Efraim & F. Sondheimer*, Tetrahedron Lett. *1963*, 313; *C.M. Bowes, D.F. Montecalvo & F. Sondheimer*, Tetrahedron Lett. *1973*, 3181.

[6] *M. Bartmann*, Ph.D. Thesis, University of Bochum.

[7] *M. Gisin & J. Wirz*, Helv. Chim Acta *59*, 2273 (1976).

[8] *R.P. Thummel, W.E. Cravey & Nutalene*, J. Org. Chem. *43*, 2473 (1978); *A.T. Blomquist & J.A. Verdol*, J. Am. Chem. Soc. *77*, 1806 (1955); *R.O. Angus & R.P. Johnson*, J. Org. Chem. *48*, 273 (1983).

[9] *W.E. Billups, E.W. Casserly & B.E. Arney, Jr.*, J. Am. Chem. Soc. *1983*, submitted for publication.

[10] *D. Davalian, P.J. Garratt, W. Koller & M.M. Mansuri*, J. Org. Chem. *45*, 4183 (1980).

[11] *B.H. Han & P. Boudjouk*, J. Org. Chem. *47*, 751 (1982); *Y. Ito, Y. Amino, M. Nakatsuka & T. Saegusa*, J. Am. Chem. Soc. *105*, 1586 (1983).