110. Synthesis of 1*H*-Cyclopropa[*b*]naphthalenes *via* Trapping of *o*-Benzoquinodimethanes

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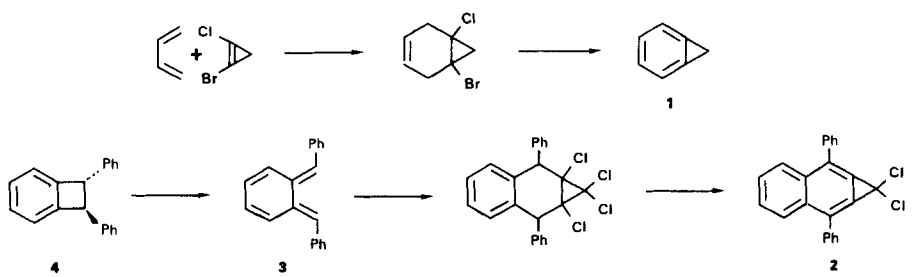
(1.IV.85)

1*H*-Cyclopropa[*b*]naphthalene (**10a**) and 3-methyl or dimethyl derivatives have been synthesized by interception of appropriately substituted *o*-quinodimethanes **3** with 1-bromo-2-chlorocyclopropene **5**, and subsequent dehydrohalogenation of the adducts. The *o*-quinodimethane derivatives **3** in turn were obtained from the diynes **7** *via* base-induced isomerization to bisallenes **8** and thermal electrocyclic ring closure.

One of the earliest approaches towards 1*H*-cyclopropabenzene (**1**) consists in cycloaddition of butadiene to a di- or tetrahalogenocyclopropene followed by dehydrohalogenation with base *(Scheme 1)* [1]. In principle, the route may be extended to synthesis of the benzannellated homologues, cyclopropa[*b*]naphthalenes. However, only 1,1-dichloro-2,7-diphenylcyclopropa[*b*]naphthalene (**2**) has been prepared in this way [2], since the *o*-quinodimethane **3**, required for the cycloaddition, was readily available from *trans*-1,2-diphenylbenzocyclobutene (**4**) *via* electrocyclic ring opening [3]. In general, however, the conditions used for generation of *o*-benzoquinodimethanes are not compatible with the presence of the very sensitive halogenocyclopropenes.

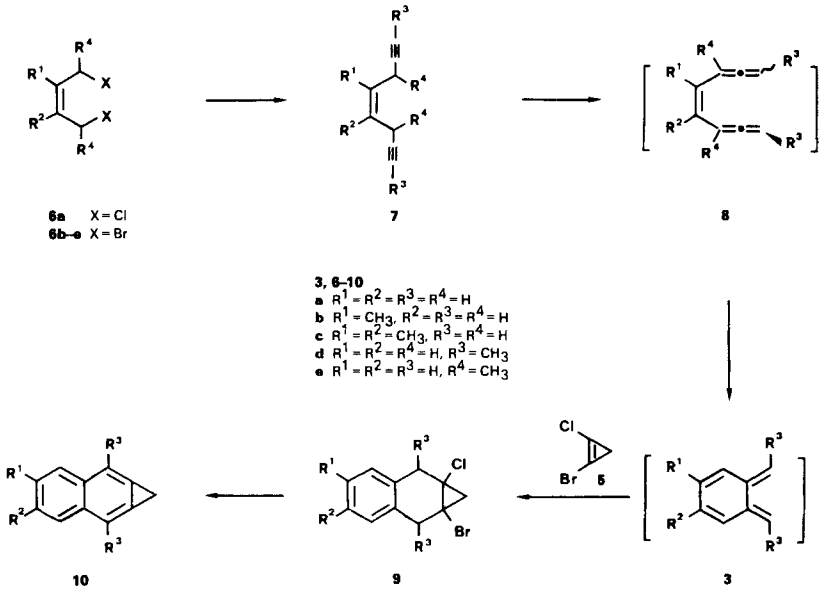
Scheme 1



Recently, we reported that *o*-naphthoquinodimethane, generated from *o*-dipropargylbenzene [4] is intercepted with 1,2-dihalogeno- and tetrahalogenocyclopropenes [5]. The adducts can be transformed to cycloprop[*b*]anthracene and its 1,1-dihalogeno derivatives. Although preliminary experiments with *o*-benzoquinodimethane (**3a**) and tetrahalogenocyclopropenes afforded no cycloadducts, we found subsequently that the more reactive 1-bromo-2-chlorocyclopropene (**5**) [6] is moderately efficient in the cycloaddition to **3a**. In this communication, we report the application of the sequence towards an alternative synthesis of 1*H*-cyclopropa[*b*]naphthalene (**10**) [7] and some of its methyl derivatives.

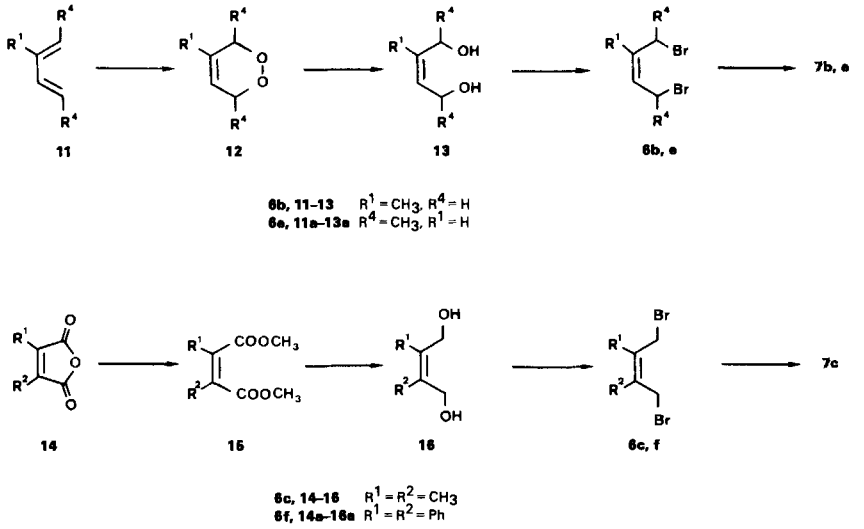
The sequence is outlined in *Scheme 2*. The required *o*-benzoquinodimethanes **3** were synthesized by the same procedure as used for the benzannellated homologues, namely by base-induced isomerization of the (*Z*)-diynes **7** to allenes **8** which underwent electrocyclic ring closure to **3** at low temperature [4]. Cycloaddition to **5** occurred in 20–50% yield upon warming of solutions containing **8** to room temperature, except in the case of **7e**, where no product could be isolated. A considerable variety of other methods of generation of *o*-benzoquinodimethane was tried [8], but none afforded cyclo-adducts with **5**. Finally, 1*H*-cyclopropa[*b*]naphthalenes **10** were obtained upon aromatization of the cyclo-adducts **9** under standard conditions (*t*-BuOK in THF) [9].

Scheme 2



The required octen-diynes **7** were obtained as follows (*Schemes 2* and *3*). Reaction of commercially available *cis*-1,4-dichloro-2-butene with ethynylmagnesium bromide or propinyllithium in presence of CuI afforded **7a** and **7d**, respectively. The 4-methyl (**7b**) and 3,6-dimethyl derivatives (**7e**) were accessible from isoprene (**11**) and (2*E*,4*E*)-2,4-hexadiene (**11a**) *via* addition of singlet oxygen [10] followed by reduction with $LiAlH_4$ [11]. The diols **13** and **13a** reacted with PBr_3 [12] to afford the dibromides **6b** and **6e**. The latter were converted with ethynylmagnesium bromide to **7b** and **7e** [4], respectively. The synthesis of (*Z*)-4,5-dimethyloct-4-ene-1,6-diyne **7c** starts with dimethylmaleic anhydride (**14**) which is transformed to the diester **15** [13]. Reduction of the ester functions to **16** with preservation of the double bond is possible with (diisobutyl)aluminium hydride/BuLi [14]. The subsequent transformations to **6c** and **7c** were carried out as described for **6b**. The same sequence, when applied to diphenylmaleic anhydride (**14a**), failed; the reaction of the dibromide **6f** with ethynylmagnesium bromide under standard conditions yielded only 2,3-diphenyl-1,3-butadiene, the product of reductive 1,4-elimination. No attempt was made to obtain the desired **7f** by modifying the procedure.

Scheme 3



The various 1*H*-cyclopropa[*b*]naphthalenes were characterized by their spectral data. The CH_3 groups appear as expected, in the range of 2.5–2.7 ppm, and the characteristic C=C stretching frequency in the IR appears at 1670–1675 cm^{-1}. The ^{13}C-NMR resonance lines are collected together with those of some reference compounds in the *Table*. The data are consistent with the structures, and they require no particular comment.

Table. *^{13}C-NMR Data of* 1H-*Cyclopropa*[b]*naphthalenes*

	C(1)	C(1a)/C(7a)	C(2)/C(7)	C(2a)/C(6a)	C(3)/C(6)	C(4)/C(5)	CH_3	CH_2	Ref.
10a	18.6	123.5	112.3	136.8	128.4	125.4			[24]
10b	18.7	123.4 122.4	112.0 111.7	136.9 135.2	127.7 127.5	134.8 128.0	21.5		This work
10c	18.6	122.4	111.3	135.4	128.2	134.8	20.0		This work
10d	18.2	120.6	117.9	136.6	124.6	124.6	16.0		This work
17	19.3	121.5	112.7	144.3	122.1	136.2		29.3	[25]
18	19.9	122.8	113.5	140.1	113.5	122.8			[26]

Financial support by the *Swiss National Science Foundation* (Project No. 2.034-0.83 is gratefully acknowledged. The authors are indebted to Prof. *W. R. Roth*, Bochum, for the detailed experimental procedure for preparation of *o*-benzoquinodimethanes **3**.

Experimental Part

General. See [9].

1. Synthesis of (*Z*)-Diynes 7. – a) *4-Methyl-1,2-dioxane* (**12**). A soln. of 10 g (147 mmol) of isoprene (**11**) in 500 ml of CH_2Cl_2 is irradiated during 8 h at 0° in presence of 60 mg of methylene blue with a 500-W tungsten lamp under a current of O_2. The soln. is then concentrated to *ca.* 5 ml and filtered through a column of *Florisil*. After concentration, 3.85 g (26%) of crude **12** [10] is obtained. ^{1}H-NMR ($CDCl_3$): 5.6 (*m*, 1H); 4.6–4.2 (*m*, 4H); 1.7 (*m*, 3H).

b) *3,6-Dimethyl-1,2-dioxane* (**12a**). The same procedure starting with 3.5 g of (2*E*,4*E*)-2,4-hexadiene afforded after 23 h 4.2 g (87%) of **12a**. ^{1}H-NMR: 5.80 (*s*, 2H); 4.50 (*q*, ^3J = 7, 2H); 1.30 (*d*, ^3J = 7, 6H).

c) *(Z)-2-Methyl-2-buten-1,4-diol* (**13**) [15]. To 3.5 g of $LiAlH_4$ in 100 ml of Et_2O was added dropwise, at 0°, 3.4 g (34 mmol) of **12** in 50 ml of Et_2O. The mixture was allowed to warm up to r.t. under N_2. After hydrolysis (10% $NaHSO_4$) and filtration, the filtrate was extracted continuously with CH_2Cl_2 during 2 d. After concentration, pure diol **13** (2.40 g, 69%) was obtained by column chromatography using silica gel and AcOEt. IR: 3600*s*, 3400 (br.), 3000–2880*m*, 1450*w*. ^{1}H-NMR ($CDCl_3$): 5.60 (*t*, 1H); 4.20 (*m*, 4H); 3.80 (*s*, 2H); 1.90 (*d*, 3H). MS: 102 (9, M^+), 84 (52), 71 (68), 55 (100), 53 (47).

d) *(Z)-3-Hexene-2,5-diol* (**13a**) [16]. The same procedure, followed by extraction during 72 h afforded diol **13a** (87%). IR: 3560*m*, 3350 (br.), 2960–2880*m*, 1450*w*, 1370*s*, 1300 (br.), 1250 (br.). ^{1}H-NMR ($CDCl_3$): 5.28–5.45 (*m*, 2H); 4.40–4.85 (*m*, 2H); 3.6 (br. *s*, 2H); 1.2 (*d*, 6H).

e) *Dimethyl (Z)-Dimethylmaleate* (**15**) [17]. Dimethylmaleic anhydride (**14**; 1.26 g, 10 mmol) in 11 g of MeOH was refluxed with methyl orthoformiate (1.4 g, 13.2 mmol) and 0.25 g of TsOH during 60 h [13]. The mixture was poured into cold H_2O and extracted with CH_2Cl_2. After usual workup, **15** was purified by column chromatography on silica gel with hexane/Et_2O 1:1. Yield 1.20 g (70%). IR ($CHCl_3$): 1720*s*, 1650*m*, 1430*w*, 1300v*s*, 1200 *m*, 1100*s*. ^{1}H-NMR ($CDCl_3$): 3.75 (*s*, 6H); 1.95 (*s*, 6H). MS: 172 (6, M^+), 141 (56), 113 (32), 85 (100).

f) *Dimethyl (Z)-Diphenylmaleate* (**15a**) [18]. The same procedure applied to diphenylmaleic anhydride (**14a**) (12.5 g) during 120 h afforded 3.3 g (22%) of **15a** and 6.0 g of unreacted **14a**. *Data of* **15a**: m.p. 108–9°. IR ($CHCl_3$): 3000–2940*m*, 1700 (br.), 1430*m*, 1250 (br.), 1050*m*, 1000*m*. ^{1}H-NMR ($CDCl_3$): 7.15 (*s*, 10 H); 3.8 (*s*, 6H). MS: 296 (100, M^+), 268 (34), 237 (43), 194 (54), 178 (85), 151 (33), 59 (46).

g) *(Z)-2,3-Dimethyl-2-butene-1,4-diol* (**16**) [19]. BuLi (60 mmol) in hexane was added to 60 mmol of DIBAL in hexane at 0° under Ar. After 30 min, the soln. was cooled to −78°, and **15** (1.72 g, 10 mmol) in 10 ml of THF was added dropwise. The soln. was allowed to warm up to r.t., and stirring was continued during 15 h. After decomposition with 10% $NaHSO_4$, the mixture was filtered and the filtrate extracted continuously with CH_2Cl_2 for 24 h. Yield 1.0 g (86%) of **16**, m.p. 32–33°. IR ($CHCl_3$): 3600*m*, 3400v*s*, 1650*w*, 1450v*s*, 1380v*s*, 1200*s*, 1000v*s*. ^{1}H-NMR ($CDCl_3$): 4.05 (*s*, 4H); 3.1 (br. *s*, 2H); 1.75 (*s*, 6H). MS: 112 (M^+, absent), 98 (94), 85 (52), 69 (100).

h) *(Z)-2,3-Diphenyl-2-butene-1,4-diol* (**16a**). The procedure for **16** was applied to 2.96 g of **15a**. The crude product was purified by chromatography with silica gel and AcOEt to afford 0.6 g (25%) of **16a** and 1.9 g unreacted **15a**. *Data of* **16** [20]: m.p. 83–85°. IR ($CHCl_3$): 3550*m*, 3350 (br.), 1600*w*, 1480*m*, 1440*m*, 1000 (br.). ^{1}H-NMR ($CDCl_3$): 7.0 (*s*, 10H); 4.5 (*s*, 4H); 2.9 (br. 2H). MS: 240 (17, M^+), 222 (30), 193 (49), 178 (49), 115 (72), 105 (100), 91 (52), 77 (53), 51 (26).

i) *Synthesis of (Z)-Dibromobutenes* **6b,c** *and (Z)-Dibromohexenes* **6d,e**. – *General Procedure* [12]. To a soln. of diol (*ca.* 20–30 mmol) in 40 ml of Et_2O was added, at 0°, 2 ml of pyridine followed by PBr_3 (40–60 mmol). After 1 h, the soln. was allowed to warm up to r.t. and stirring was continued for 20 h. The mixture was poured into cold H_2O. Usual workup affords the dibromo derivatives **6b–e**. The bromides were chromatographically pure, and they were used without further treatment with the exception of **6e** (distillation) and **6f** (column chromatography).

(Z)-1,4-Dibromo-2-methylbutene (**6b**) (60% yield). IR ($CHCl_3$) [15]: 3040*w*, 1650*w*, 1450*m*, 1200v*s*, 1000*m*, 920*m*. ^{1}H-NMR ($CDCl_3$): 5.75 (*td*, 1H); 4.0 (*t*, 4H); 1.9 (*m*, 3H). MS: 230–228 (7, M^+), 149, 147 (100), 121, 119 (10), 67 (63), 41 (63).

(Z)-1,4-Dibromo-2,3-dimethyl-2-butene (**6c**) [21] (72% yield). IR ($CHCl_3$): 1640*m*, 1450*s*, 1380*s*, 1290–1270*m*, 1180*m*, 920*m*. ^{1}H-NMR ($CDCl_3$): 4.05 (*s*, 4H); 1.75 (*s*, 6H). MS: 242–240 (10, M^+), 163, 161 (100), 81 (64), 67 (46), 53 (43).

(Z)-1,4-Dibromo-2,3-diphenyl-2-butene (**6f**) (56% yield), m.p. 84–85°. IR ($CHCl_3$): 3080*m*, 3060*m*, 3000*m*, 1600*w*, 1490*m*, 1450*m*, 1280*m*, 1000 (br.), 700*w*. ^{1}H-NMR ($CDCl_3$): 7.10 (*s*, 10H); 4.50 (*s*, 4H). MS: 366 (3, M^+), 287 (3), 205 (100), 191 (10), 178 (10), 128 (15), 115 (12), 101 (28), 91 (36), 77 (28), 51 (26).

(Z)-2,5-Dibromo-3-hexene (**6e**) (16% yield). IR ($CHCl_3$): 3020*s*, 1530*w*, 1445*w*, 1380*w*, 1220v*s*, 1145*m*, 1025*w*, 925*w*. ^{1}H-NMR ($CDCl_3$): 5.5–5.7 (*m*, 2H); 4.8–5.2 (*m*, 2H); 1.80 (*d*, 6H). MS: 242 (1, M^+), 175 (1), 163, 161 (63), 135, 133 (8), 119, 117 (9), 81 (100), 67 (82), 53 (93).

j) *(Z)-Diynes* **7**. – *General Procedure.* To ethynylmagnesium bromide in THF, prepared from 90 g of bromoethane and 18 g of Mg followed by introduction of acetylene, was added 2.0 g (13.3 mmol) of NaI and 3.0 g (23.3 mmol) of CuCl. The mixture was heated to 50°, and the dihalide (**6a–e**) (20–60 mmol) in 50 ml of THF was added. After 18 h at 50°, the mixture was poured into ice. Usual workup afforded the crude products (**7a–e**).

(Z)-4-Octene-1,7-diyne (**7a**). Yield 20% after distillation (50°/20 Torr). IR ($CHCl_3$): 3280*vs*, 2900*w*, 2100*w*, 1420*w*, 1200 (br.). ^{1}H-NMR ($CDCl_3$, 100 MHz): 5.50 (*m*, 2H); 3.0 (*t*, 4H); 2.0 (*t*, 2H).

(Z)-4-Methyl-4-octene-1,7-diyne (**7b**). Yield 40% (crude). ^{1}H-NMR ($CDCl_3$): 5.5–5.0 (*m*, 1H); 3.0 (*d*, 4H); 2.0 (*t*, 2H); 1.85 (*d*, 3H). IR ($CHCl_3$): 3300*s*, 2980–2860*s*, 2120*w*, 1450*m*, 1260*m*, 1100–1000 (br.), 750 (br.).

(Z)-4,5-Dimethyl-4-octene-1,7-diyne (**7c**). Yield 66% (crude). IR ($CHCl_3$): 3260*vs*, 2900–2840*s*, 2100*m*, 1420*s*, 1380*m*, 1220 (br.), 1080*w*, 900*w*. ^{1}H-NMR ($CDCl_3$): 2.9 (*d*, 4H); 1.9 (*t*, 2H); 1.8 (*s*, 6H). MS: 132 (19, M^+), 131 (19), 117 (84), 91 (100), 77 (90), 65 (38), 51 (36).

(Z)-5-Decene-2,8-diyne (**7d**). The same procedure was applied starting with commercially available proninyllithium and **6a**. Yield 38%, after chromatography on silica gel with hexane/CH_2Cl_2 4:1. IR ($CHCl_3$): 3000–2860*w*, 2220*m*, 1430*s*, 1380*s*, 1200 (br.). ^{1}H-NMR ($CDCl_3$): 5.45 (*t*, 2H); 2.85 (*m*, 4H); 1.8 (*m*, 6H).

(Z)-3,6-Dimethyl-4-octene-1,7-diyne (**7e**). Yield 40% (crude). IR ($CHCl_3$): 3300*s*, 2980–2860*m*, 2120*w*, 1450*m*, 1380*m*, 1260*m*, 970*s*. ^{1}H-NMR ($CDCl_3$): 5.45–5.8 (*m*, 2H); 3–3.5 (*m*, 2H); 2.1–2.3 (*m*, 2H); 1.75 (*d*, 6H).

2. Generation and Interception of *o*-Benzoquinodimethanes 3a–d. The diynes **7** were isomerized to the corresponding bis-allenes **8** by treatment with *t*-BuOK at –78° [4]. The detailed procedure is described in [24]. To the solns. containing the bis-allenes was added, at –78°, an excess of freshly prepared 1-bromo-2-chlorocyclopropene (**5**) [25] in THF. After 2 h at –78°, the soln. was allowed to warm up to r.t. The mixture was treated with H_2O and then extracted with hexane. Chromatography with silica gel using $CHCl_3$ as eluant afforded the cyclo-adducts **9a–d**. No addition product was obtained from **7e**.

*1a-Bromo-7a-chloro-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene* (**9a**). Yield 47%, m.p. 44–45°. IR ($CHCl_3$): 3040–3000*w*, 2900–2800*w*, 1585*w*, 1490*m*, 1420*m*, 1070*s*, 1020 (br.), 830*w*. ^{1}H-NMR ($CDCl_3$): 7.4–7.0 (*m*, 4H); 3.55 (*m*, 4H); 1.35 (*m*, 2H). MS: 258–256 (15, M^+), 223–221 (12), 179–177 (60), 141–140 (100).

*1a-Bromo-7a-chloro-4-methyl-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene* (**9b**). Yield 30% (liq). IR ($CHCl_3$): 3080–3020*w*, 2950–2820*s*, 1620*w*, 1510*m*, 1420*m*, 1080*s*, 810*s*. ^{1}H-NMR ($CDCl_3$, 100 MHz): 7.0 (*s*, 2H); 6.9 (*s*, 1H); 3.5 (*m*, 4H); 2.35 (*s*, 2H); 1.4 (*m*, 2H). MS: 272–270 (7, M^+), 244–242 (10), 193–192 (19), 191 (42), 157 (33), 156 (48), 155 (100), 141 (40), 115 (40).

*1a-Bromo-7a-chloro-4,5-dimethyl-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene* (**9c**). Yield 46%, m.p. 103–105°. IR ($CHCl_3$): 3010*w*, 2960–2840*m*, 1510*w*, 1450 (br.), 1310*w*, 1080*s*, 1030*w*, 880*w*. ^{1}H-NMR ($CDCl_3$, 100 MHz): 6.8 (*s*, 2H); 3.5 (*m*, 4H); 2.2 (*s*, 6H); 1.3 (*m*, 2H). MS: 286–284 (20, M^+), 207–205 (50), 169 (100), 155 (44), 115 (37).

*1a-Bromo-7a-chloro-2,7-dimethyl-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene* (**9d**). Yield 19%, m.p. 35–36°. IR ($CHCl_3$): 3000–2960*m*, 2940–2880*w*, 1700*w*, 1600*w*, 1490*m*, 1460*m*, 1380*m*, 1260*m*, 1220 (br.), 1100–1000*m*, 750*w*, 680*w*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.4–7.2 (*m*, 4H); 3.6 (*m*, 2H); 1.8–1.5 (*m*, 6H); 1.3 (*m*, 2H). MS: 286 (9, M^+), 271 (15), 249 (9), 221 (15), 205 (100), 187 (15), 177 (15), 169 (62), 155 (40), 128 (27), 76 (22).

3. Preparation of 1*H*-Cyclopropa[*b*]naphthalenes 10a–d. – *General Procedure.* The precursors **9** in THF were treated at –78° with 5–6 mol-equiv. of *t*-BuOK in THF. After 2 h at –78°, the reaction was allowed to warm up to r.t. The solvent was evaporated and the residue was extracted with pentane. The 1*H*-cyclopropa[*b*]naphthalenes **10** were obtained as yellow crystals upon concentration of the solvent.

*1*H*-Cyclopropa[*b*]naphthalene* (**10a**). Yield 98%. The physical and spectral data are identical with those reported in [7] [24].

*4-Methyl-1*H*-cyclopropa[*b*]naphthalene* (**10b**). Quant., yield m.p. 40°. IR: 1670 (C=C). ^{1}H-NMR ($CDCl_3$, 100 MHz): 7.85 and 7.35 (*m*, 2H); 7.70 (*s*, 1H); 7.50 (*d*, 2H); 3.55 (*s*, 2H); 2.55 (*s*, 3H). MS: 154 (100, M^+), 139 (33), 128 (11), 115 (11), 76 (25), 71 (9), 63 (16), 57 (13), 51 (13).

*4,5-Dimethyl-1*H*-cyclopropa[*b*]naphthalene* (**10c**). Yield 85% after chromatography on silica gel with hexane/CH_2Cl_2 3:1, m.p. 118–120°. IR: 1675 (C=C). ^{1}H-NMR ($CDCl_3$, 100 MHz): 7.65 (*s*, 2H); 7.5 (*s*, 2H); 3.50 (*s*, 2H); 2.45 (*s*, 6H). MS: 168 (100, M^+), 153 (43), 152 (50), 134 (6), 139 (6), 115 (6), 76 (9), 63 (7), 51 (6).

*2,7-Dimethyl-1*H*-cyclopropa[*b*]naphthalene* (**10d**). Quant. yield, m.p. 45–46°. IR: 1675 (C=C). ^{1}H-NMR ($CDCl_3$, 360 MHz): 8.05 (*m*, 2H); 7.50 (*m*, 2H); 3.40 (*s*, 2H); 2.70 (*s*, 6H). MS: 168 (100, M^+), 153 (90), 141 (10), 128 (10), 115 (14), 83 (14), 76 (11), 51 (9).

REFERENCES

[1] E. Vogel, S. Korte, W. Grimme, H. Günther, *Angew. Chem. Int. Ed.* **1968,** *7,* 289; B. Halton, *Chem. Rev.* **1973,** *73,* 113, I & EC Prod. Res. Devel. **1980,** *19,* 349; W.E. Billups, *Acc. Chem. Res.* **1978,** *11,* 245.

[2] A.R. Browne, B. Halton, *J. Chem. Soc., Chem. Commun.* **1972,** 1341; *J. Chem. Soc., Perkin Trans. 1* **1977,** 1177.

[3] R. Huisgen, H. Seidl, *Tetrahedron Lett.* **1964,** 3381.

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

[5] P. Müller, D. Rodriguez, *Helv. Chim. Acta* **1983,** *66,* 2540.

[6] W.E. Billups, L.J. Lin, B.E. Arney, Jr., W.A. Rodin, E.W. Casserly, *Tetrahedron Lett.* **1984,** *25,* 3935; W.E. Billups, E.W. Casserly, B.E. Arney, Jr., *J. Am. Chem. Soc.* **1984,** *106,* 440.

[7] W.E. Billups, W.Y. Chow, *J. Am. Chem. Soc.* **1973,** *95,* 4099.

[8] K. Alder, M. Fremery, Tetrahedron **1961,** *14,* 190; B. Hee Han, P. Bondjouk, *J. Org. Chem.* **1982,** *47,* 751; Y. Ito, M. Nakabuka, T. Saegussa, *J. Am. Chem. Soc.* **1982,** *104,* 7609.

[9] P. Müller, M. Rey, *Helv. Chim. Acta* **1982,** *65,* 1157.

[10] K. Kondo, M. Matsumoto, *J. Chem. Soc., Chem. Commun.* **1972,** 1332.

[11] M. Balci, *Chem. Rev.* **1981,** *81,* 91; G. Rio, J. Berthelot, *Bull. Soc. Chim. Fr.* **1969,** 1664; G.O. Schenck, D.E. Dunlap, *Angew. Chem.* **1956,** *68,* 248; C. Kaneko, A. Sugimoto, S. Tanaka, *Synthesis* **1974,** 876.

[12] F. Delay, G. Ohloff, *Helv. Chim. Acta* **1979,** *62,* 369; C.W. Doeck, P.J. Garratt, H. Ghahriari-Zavareh, R. Zahler, *J. Org. Chem.* **1984,** *49,* 1412.

[13] J.J. Bloomfield, S.L. Lee, *J. Org. Chem.* **1967,** *32,* 3919.

[14] S. Kim, K.H. Ahn, *J. Org. Chem.* **1984,** *49,* 1717; T.K. Chakraborty, S. Chandrasekaran, *Tetrahedron Lett.* **1984,** *25,* 2891; H. Nishinyama, M. Sasaki, K. Itoh, *Chem. Lett. Jpn.* **1981,** 1363; G. Kovacs, G. Galambos, Z. Juvancj, *Synthesis* **1977,** 171.

[15] V.L. Heasley, C.L. Frye, R.T. Gore, Jr., P.S. Wildeny, *J. Org. Chem.* **1968,** *33,* 2342.

[16] J.P. Gentet, M. Balabanc, Y. Legras, *Tetrahedron Lett.* **1982,** *23,* 331; W. Reppe, *Liebigs Ann. Chem.* **1955,** *596,* 44.

[17] C. Girard, R. Bloch, *Tetrahedron Lett.* **1982,** *23,* 3683; K.V. Auwers, E. Cauer, *Liebigs Ann. Chem.* **1929,** *470,* 284.

[18] H. Fauduet, R. Burgada, *Nouv. J. Chem.* **1980,** *4,* 113; M. Ramart-Lucas, M.J. Hoch, *Ann. Chim.* **1980,** *14,* 395.

[19] N. Frederiksen, R.B. Jensen, S.E. Jorgensen, J.U.R. Nielsen, L. Nørskov, G. Schroll, *Acta. Chem. Scand., Ser. B* **1977,** *31,* 694.

[20] G. Rio, B. Serkig, *Bull. Soc. Chim. Fr.* **1976,** 1491; J. Tsui, T. Nogi, *J. Am. Chem. Soc.* **1966,** *88,* 1289.

[21] O.J. Sweeting, J.R. Johnson, *J. Am. Chem. Soc.* **1946,** *68,* 1057.

[22] M. Bartmann, Ph.D. Thesis, University of Bochum, 1980.

[23] W.E. Billups, L.J. Lin, B.E. Arney, Jr., W.A. Rodin, E.W. Casserly, *Tetrahedron Lett.* **1984,** *25,* 3935.

[24] H. Günther, G. Zikeli, H. Schmickler, J. Prestien, *Angew. Chem.* **1973,** *85,* 826.

[25] D. Davalian, P.J. Garratt, *Tetrahedron Lett.* **1976,** *17,* 2815.

[26] J. Ippen, E. Vogel, *Angew. Chem. Int. Ed.* **1974,** *13,* 736.