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UNSATURATED MACROCYCLIC COMPOUNDS—LII[1]

THE SYNTHESIS OF 1,8-DIETHYNYLNAPHTHALENE AND ITS OXIDATION TO A CONJUGATED FOURTEEN-MEMBERED RING SYSTEM

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Abstract—A seven step synthesis of 1,8-diethynylnaphthalene (IX) from naphthalic anhydride (I) is described. Oxidation of IX with oxygen, cuprous chloride and ammonium chloride gave the very unstable "cyclic dimer" (XX), containing a conjugated 14-membered ring.

1,8-DIETHYNYLNAPHTHALENE (IX) appeared to be a valuable intermediate for the synthesis of conjugated macrocyclic compounds containing fused naphthalene nuclei. We now describe a convenient synthesis of IX, and its oxidative coupling to the corresponding "cyclic dimer" (XX), containing a conjugated 14-membered ring.

The starting material was the commercially available naphthalic anhydride (I), which was reduced with LAH to 1,8-bis(hydroxymethyl)naphthalene (II) in 66% yield.[3] Treatment of II with phosphorus tribromide and pyridine in ether led to 93% of the dibromide III,[4,5] which was converted in 87% yield to the corresponding bis-triphenylphosphonium salt IV by treatment with 2 molar equivalents of triphenylphosphine in boiling dimethylformamide.* Excess sodamide in liquid ammonia transformed IV to the bis-ylide V, which on Wittig reaction with gaseous formaldehyde in boiling ether gave 1,8-divinylnaphthalene (VI) in 87% yield. The diene VI has been prepared previously (in 70% yield) by the Wittig reaction of 1,8-naphthalenedicarboxaldehyde hydrate (VII) with triphenylphosphine-methylene,[8] but the presently described method is preferred since the diol II is more readily available in quantity than the dialdehyde hydrate VII.

Reaction of 1,8-divinylnaphthalene (VI) with excess bromine in carbon tetrachloride gave the tetrabromide VIII in essentially quantitative yield. The complexity of the NMR spectrum (Experimental) indicated that VIII was a stereoisomeric mixture. The dehydrobromination of VIII to 1,8-diethynylnaphthalene (IX) caused some difficulties, but after some experimentation it was found that this transformation could be effected in 79% yield by means of potassium t-butoxide in boiling t-butanol and dioxan. The over-all yield in the seven steps from I was ca. 37%.

The diacetylene IX proved to be a rather unstable substance. The structural assignment was based on the elemental analysis, as well as the IR, NMR and mass spectra. The structure was confirmed by catalytic hydrogenation in ethyl acetate over a platinum catalyst, whereby 73% of 1,8-diethylnaphthalene (X) and 24% of 1,8-diethyltetralin (XI) were obtained. The same two substances X and XI were formed in about the same yield by the analogous hydrogenation of 1,8-divinylnaphthalene (VI).

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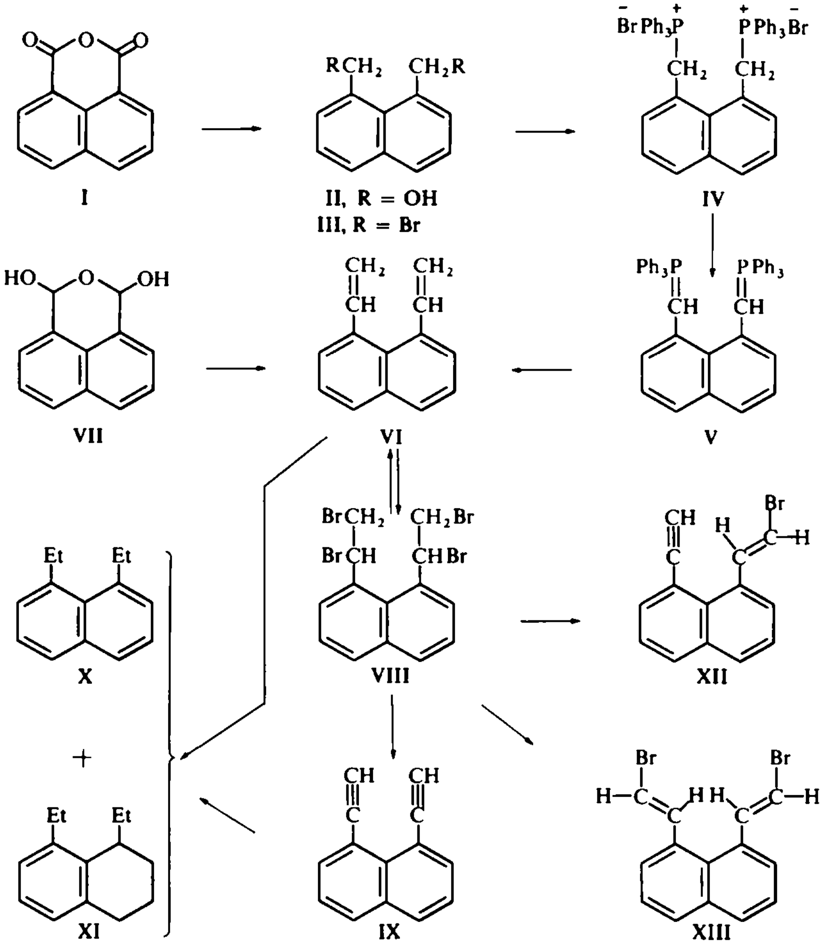
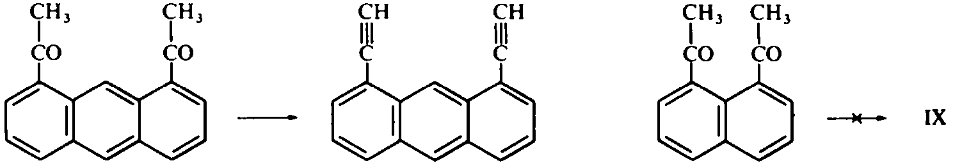
* The synthesis of the bis-triphenylphosphonium salt IV has now been described by other workers.[6,7]



The diacetylene IX was not obtained when the dehydrobromination of the tetrabromide VIII with potassium t-butoxide in t-butanol and dioxan was carried out at room temperature. Instead, this reaction gave rise to 64% of 1-(*trans*-β-bromovinyl)-8-ethynylnaphthalene (XII) as well as to 28% of 1,8-bis(*trans*-β-bromovinyl)-naphthalene (XIII). These structures are based on the elemental analyses and spectroscopic evidence; the *trans*-configuration of the double bonds is indicated by the facts that strong bands at ca. 950 cm^{-1} were apparent in the IR spectra of both substances, while the olefinic protons in the NMR spectra showed $J = 14$ c/s (Experimental).

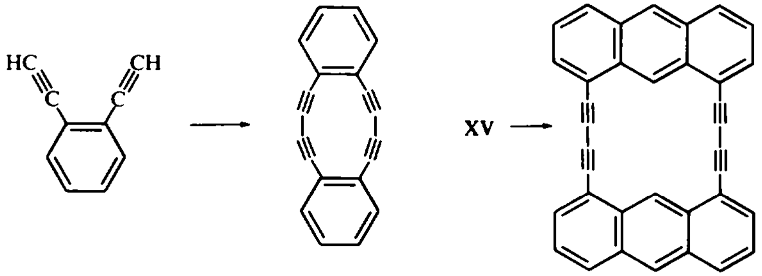
Treatment of the tetrabromide VIII with excess sodamide in liquid ammonia regenerated 1,8-divinylnaphthalene (VI) in 61% yield, debromination rather than dehydrobromination having occurred. Similar observations have been made with related compounds.[9, 10]

It has been shown that 1,8-diethynylanthracene (XV) can be prepared from 1,8-diacetylanthracene (XIV) by chlorination with phosphorus pentachloride in phosphorus oxychloride, followed by dehydrochlorination with sodamide in liquid



ammonia.[11] By analogy, 1,8-diacetylnaphthalene (XVI)[8] was subjected to this reaction sequence, before the above-described route to IX was developed, but no IX could be isolated.

A variety of terminal diacetylenes have been oxidized to the corresponding cyclic dimers, as well as to other cyclic oligomers, by means of cupric acetate in pyridine ("Eglinton conditions") or oxygen, cuprous chloride and ammonium chloride in aqueous ethanol ("Glaser conditions").[12] For instance, *o*-diethynylbenzene (XVII) on oxidation under the Eglinton conditions gave the cyclic dimer XVIII in 43% yield,[9] while 1,8-diethynylanthracene (XV) gave the cyclic dimer XIX in 95% yield



XVII XVIII XIX

under these conditions.[11] The very high yield of XIX is presumably due to the fact that the precursor XV contains rigid parallel ethynyl groupings. 1,8-Diethynylnaphthalene (IX) possesses the same feature, and oxidation of this substance was therefore expected to proceed smoothly to give the cyclic dimer XX.

In the event, the oxidative coupling of IX to the cyclic dimer XX could be effected, though only in poor yield. The best yield of XX (ca. 2%) was obtained when IX was oxidized under the Glaser conditions in the presence of benzene,* while Eglinton conditions at best gave only traces of XX.† The red cyclic dimer XX proved to be a very unstable substance, and it could be kept at room temperature only in relatively dilute solution for less than 1 hr. All attempts to obtain XX in the neat state or in concentrated solution resulted in decomposition, and it was not possible to determine the IR, NMR or mass spectrum. The UV spectrum of XX in pentane–ether (given in Fig. 1, together with the UV spectrum of IX) exhibited λ_{max} 328 mμ (log ε 4·00), 502 (3·46) and 540 (3·67).‡

The structure of XX is based on the fact that it contains no terminal acetylene

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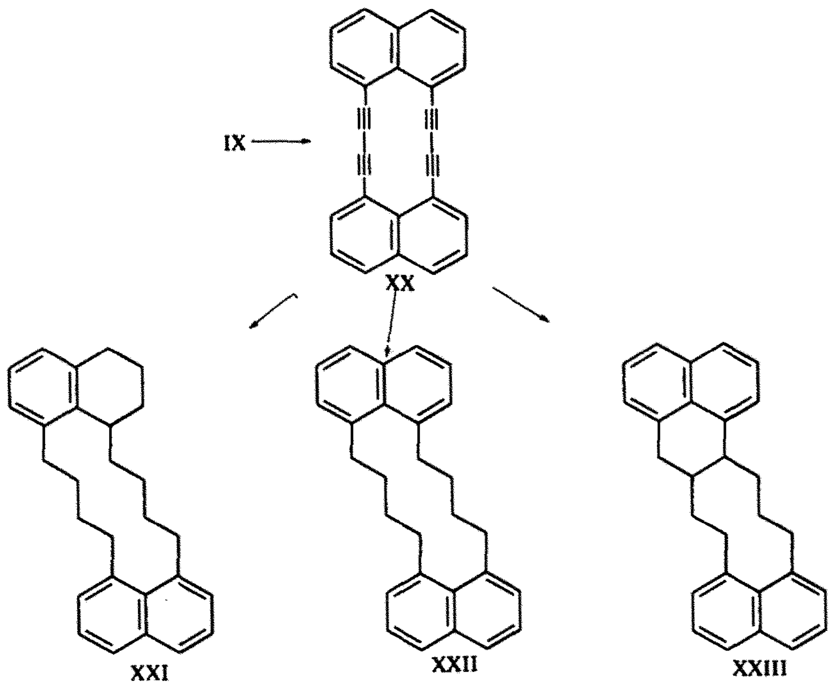
* The benzene serves to keep the products in solution.[13]

† The low yield of XX may be due to the fact that the di-cuprous derivative of IX was found to be very unstable, rapidly giving a black material on exposure to air. The same reason has been suggested for the rather poor yield of cyclic dimer obtained by the coupling of 1,8-bis-butadiynylanthracene.[14]

‡ The true ε values must be considerably higher, since black polymeric material separated during determination of the UV spectrum. The reported values were estimated from the weight obtained after catalytic hydrogenation.



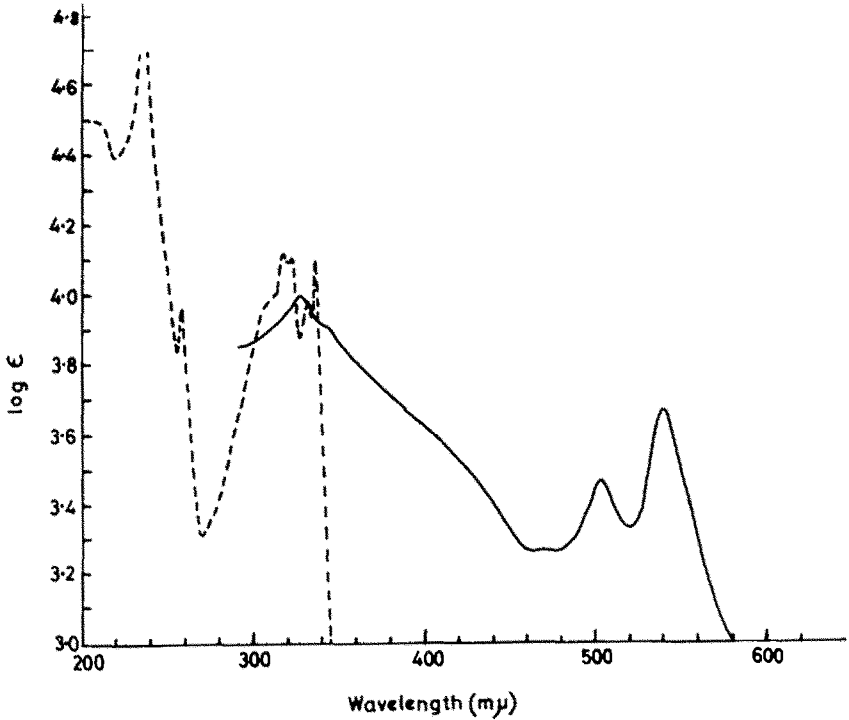


Fig. 1 UV absorption spectra of 1,8-diethynylnaphthalene, IX (broken line) and of "cyclic dimer" XX (solid line).*

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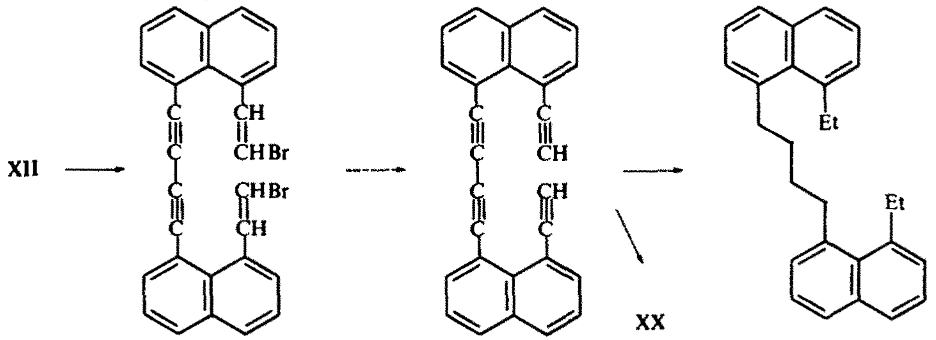
* See footnote ‡, page 1399.

(since XX was isolated after the crude coupling product had been shaken with alcoholic silver nitrate), and on the results of catalytic hydrogenation. The hydrogenation of XX in ethyl acetate over a platinum catalyst gave a mixture of three substances, separated by preparative TLC. The first two (in order of elution) are assigned the naphthalene-tetralin structure XXI and the dinaphthalene structure XXII, on the basis of the mass spectra (M = 368 and 364, respectively); the UV spectra were in accord with these formulations. The mass spectrum of the third substance (M = 362) showed that it contained two protons less than XXII, and it probably possesses a hexacyclic dinaphthalene structure (e.g. XXIII) formed by a transannular reaction. It is noteworthy that mass spectral examination of the hydrogenation products indicated the absence of the diethyl compound XXVI (M = 366), which would have been formed from the linear dimer XXV.

The extreme instability of the cyclic dimer XX is presumably due to the proximity of the two 1,3-diyne groupings. By comparison, the benzene analogue XVIII is moderately stable,[9] and the anthracene analogue XIX is very stable.[11]

An alternative route to the cyclic tetra-acetylene XX was studied, involving the oxidative coupling of the bromovinyl-acetylene XII to the 1,3-diyne XXIV; dehydrobromination to XXV and repeated coupling was then expected to give XX. However, the oxidation of XII to XXIV proceeded only in very poor yield, and this route was therefore not pursued further.



XXIV XXV XXVI

The synthesis of other conjugated macrocycles from 1,8-diethynylnaphthalene (IX) is now under investigation.

EXPERIMENTAL

M.ps were taken on a Kofler block and are uncorrected. IR spectra: as KBr discs on a Perkin–Elmer 257

otherwise stated) on a Cary model 14M spectrophotometer. NMR spectra: on a Perkin–Elmer R.10 or a Varian HA-100 instrument, TMS being used as an internal standard. Mass spectra: on an AEI MS9 mass spectrometer (direct inlet system).

1,8-*Bis(bromomethyl)naphthalene* (III)

1,8-Bis(hydroxymethyl)naphthalene (II) was prepared in 66% yield by reduction of I (Koch-Light Ltd) with LAH, essentially as described by Beyler and Sarett.[3] PBr_3 (100 g, 0·37 mole) in dry ether (1 l.) was added dropwise during 1 hr to a stirred suspension of II (48·7 g, 0·26 mole) in dry ether (2 l.) containing pyridine (10 ml, dried over CaH_2). The mixture was stirred for 48 hr, and was then poured into H_2O. The ether layer was washed with $NaHCO_3$ aq, dried and evaporated. Crystallization from ether gave III (75·3 g, 93%), m.p. 131–132° (lit m.p. 129–130°,[4] 130–131·5°[5]). (Found: C, 46·05; H, 3·5; Br, 50·5. Calc. for $C_{12}H_{10}Br_2$: C, 45·9; H, 3·2; Br, 50·9%); λ_{max} 226 mμ (log ε 4·72) and 297 (3·90). This procedure was superior to those described previously, in which no pyridine (75% yield)[4] or a few drops of pyridine (81% yield)[5] was used.

1,8-*Bis(triphenylphosphoniomethyl)naphthalene dibromide* (IV)

A soln of III (122 g, 0·39 mole) and triphenylphosphine (210 g, 0·80 mole) in dimethylformamide (1 l.) was boiled under reflux for 3 hr, and then stirred for 14 hr without further heating. The ppt was collected, washed with dimethylformamide and dry ether, and was then dried. The resulting IV (284 g, 87%) showed m.p. 325–326° (lit. m.p. > 300°,[6] 311–313°[7]). (Found: C, 68·9; H, 4·8; Br, 18·8; P, 7·65. Calc. for $C_{48}H_{40}Br_2P_2$: C, 68·75; H, 4·8; Br, 19·05; P, 7·4%); ν_{max} 1445, 1115, 775, 760, 745, 725 and 695 cm^{-1}; λ_{max} 269 mμ (log ε 4·03), 277 (3·99) and 299 (3·82); NMR spectrum (CD_3OD), 36 H multiplet at τ 2·0–2·6 (aromatic protons) and 4H multiplet at τ 2·75–2·96 (methylene protons).

1,8-*Divinylnaphthalene* (VI)

NH_3 (dried by passage through KOH) was passed into a 5 l. 3-neck flask (equipped with a gas inlet tube, stirrer and reflux condenser) cooled with CO_2-acetone, until ca. 2·5 l. had condensed. The cooling bath was removed, powdered $NaNH_2$ (10·0 g, 0·256 mole) was added, followed by powdered IV (80 g, 0·095 mole). The mixture was stirred without further cooling for 1 hr under N_2. Dry ether (3 l.) was then added gradually during 2 hr, the NH_3 being evaporated. The resulting bright scarlet soln of the bis-ylide V was boiled under reflux for 1 hr in N_2 (to remove all NH_3), more ether being added occasionally to maintain the original volume. Dry gaseous formaldehyde (generated by the pyrolysis of dry paraformaldehyde at 180–200°)[15] in a N_2 stream was led into the flask above the surface of the boiling liquid, until the red ylide colour was discharged (ca. 30 min). The mixture was then boiled under reflux for 15 min, cooled and poured into H_2O. The ether layer was washed with 2N HCl and H_2O, and the dried extract was evaporated at 25° under reduced press. The residue was extracted with pentane, and filtered through Al_2O_3 (200 g, Camag activity I). Pentane (2 l.) eluted VI, which on crystallization from MeOH formed needles (15·0 g, 87%), m.p. 44–46° (lit[9] m.p. 47–47·5°); ν_{max} 998, 925, 908, 840, 798, 780 and 685 cm^{-1}; λ_{max} 235 mμ (log ε 4·64) and 309 (3·96); NMR spectrum (CCl_4), 8H multiplet at τ 2·15–2·85 (6 aromatic protons and 2 α-vinylic protons) and 4H multiplet at τ 4·30–4·90 (β-vinylic protons); mass spectrum, peaks at *m/e* 180 (M^+; 66%), 179 (M-H; 64%), 178 (M-H_2; 24%), 166 (M-CH_2; 17%) and 165 (M-CH_3; 100%). The compound gradually decomposed on standing at room temp, and it was usually stored at ca. −15°.

1,8-*Bis(1′,2′-dibromoethyl)naphthalene* (VIII)

Br_2(27·0 g, 0·169 mole) in CCl_4 (500 ml) was added dropwise during 45 min to a soln of VI (10·0 g, 0·056 mole) in CCl_4 (500 ml) at 0°, with stirring. The mixture was stirred for a further 30 min at 0°, and then for 90 min without cooling. The soln was poured into ice-water, and the organic layer was washed with $NaHSO_3$aq until the colour of Br_2 had disappeared. The extract was washed with 2N HCl and H_2O, and was then dried and evaporated under reduced press. Trituration of the residue with pentane yielded VIII (27·7 g, 100%) as pale yellow crystals, m.p. 120–124°; homogeneous on TLC. Crystallization from pet. ether (b.p. 110–120°) gave the analytical sample as colourless crystals, m.p. 123–124°. (Found: C, 33·9; H, 2·55; Br, 63·55. $C_{14}H_{12}Br_4$ requires: C, 33·65; H, 2·4; Br, 63·95%); ν_{max} 942, 835, 765 and 675 cm^{-1}; λ_{max} 235 mμ (log ε 4·55) and 313 (3·89); NMR spectrum (CCl_4), 6H multiplet at τ 1·94–2·58 (aromatic protons), 2H multiplet at τ 3·45–4·02 (α-methine protons) and 4H multiplet at τ 5·55–5·95 (β-methylene protons);[16] mass spectrum, peaks at *m/e* 504, 502, 500, 498, 496 (M^+; 0·01, 0·05, 0·08, 0·05, 0·01%), 423, 421, 419, 417 (M-Br; 0·03, 0·08, 0·08, 0·03%), 422, 420, 418, 416 (M-HBr; 0·14, 0·42, 0·42, 0·14%), 341, 339, 337 (M-HBr_2; 0·5, 1·0, 0·5%), 260, 258 (M-HBr_3; 1·3% each), 180 (M-Br_4; 35%), 179 (M-HBr_4; 53%), 178 (M-H_2Br_4; 24%) and 165 (M-CH_3Br_4; 100%).

1,8-*Diethynylnaphthalene* (IX)

A soln of $KOBu^t$ (0·5 mole) in Bu^tOH (1 l.) [prepared from K (19·5 g)] was added during 30 min to a vigorously stirred soln of VIII (25·0 g, 0·050 mole) in dioxan (250 ml, dried over Na). The mixture was boiled under reflux for 1 hr, cooled, and the solvents were evaporated under reduced press. Ether (1 l.) and H_2O (1 l.) were then added to the dark brown residue. The aqueous phase was acidified with 3N HCl, extracted with ether, and the combined ether layers were washed with 3N HCl and H_2O. The dried extract was evaporated under reduced press, and the residue, dissolved in a little benzene, was chromatographed on Al_2O_3 (300 g; Woelm neutral, activity II–III). Elution with pentane–ether (50:1) and crystallization from pentane yielded IX (6·92 g, 79%) as plates, m.p. 73–73·5. (Found: C, 95·35; H, 4·9. $C_{14}H_8$ requires: C, 95·4; H, 4·6%); ν_{max} 3280, 2100, 1375, 835 and 770 cm^{-1}; λ_{max} 234 mμ (log ε 4·82), 257 (3·94), 306 sh (3·98), 310 sh (4·00), 316 (4·12), 321 (4·10), 330 (3·98) and 335 (4·10) (see Fig. 1); NMR spectrum (CCl_4), 6H multiplet at τ 2·10–2·80 (aromatic protons) and 2H singlet at τ 6·75 (acetylenic protons); mass spectrum, peaks at *m/e* 176 (M^+; 100%), 175 (M-H; 12%), 174 (M-2H; 11%) and 162 ($M\text{-}CH_2$; 9·5%). The substance on standing at room temp rapidly turns yellow and then brown on the surface, but it can be kept with little change for several months at −15° in the dark.

Debromination of VIII *to* VI *with sodamide in liquid ammonia*

A soln of VIII (500 mg, 1 mmole) in dry ether (40 ml) was added dropwise during 15 min to a stirred suspension of sodamide (1·5 g, 38 mmoles) in dry liq NH_3 (150 ml), without external cooling. The mixture was stirred for a further 90 min, and excess NH_4Cl was then added. Isolation with ether in the usual way, followed by crystallization from MeOH, gave VI (110 mg, 61%), m.p. 41–43°. Identity with an authentic sample was established by mixture m.p. determination and IR spectral comparison.

1-(trans-β-Bromovinyl)-8-ethynylnaphthalene (XII) *and 1,8-bis(*trans*-β-bromovinyl)naphthalene* (XIII)

A soln of $KOBu^t$ (0·3 mole) in Bu^tOH (600 ml) [prepared from K (11·7 g)] was added during 30 min to a vigorously stirred soln of VIII (20·0 g, 0·040 mole) in dioxan (300 ml). The mixture was stirred at room temp for 24 hr, and the solvents were evaporated under reduced press at 30–35°. Ether (250 ml) and water (250 ml) were added, and the organic layer was washed with 2N HCl and H_2O. The dried extract was evaporated under reduced press, and the residue, dissolved in a little benzene, was chromatographed on Al_2O_3 (500 g; Woelm neutral, activity II–III).

Pentane eluted firstly the dibromide XIII, which on crystallization from MeOH gave needles (3·80 g, 28%), m.p. 113–114°. (Found: C, 50·1; H, 3·4; Br, 46·85. $C_{14}H_{10}Br_2$ requires: C, 49·7; H, 3·0; Br, 47·3%); ν_{max} 3100, 2950, 1615, 1590, 1190, 1025, 950, 860, 820, 785 and 770 cm^{-1}; λ_{max} 234 mμ (log ε 4·60) and 310 (4·08); NMR spectrum (CCl_4), 8H multiplet at τ 2·10–2·80 (6 aromatic and 2 α-vinylic protons) and 2H doublet (J = 14 c/s) at τ 3·57 (β-vinylic protons);[17] mass spectrum, peaks at *m/e* 340, 338, 336 (M^+; 0·75, 1·5, 0·75%), 259, 257 (M-Br; 2·6% each), 258, 256 (M-HBr; 1·5% each), 178 ($M\text{-}Br_2$; 100%), 177 ($M\text{-}HBr_2$; 9%) and 176 ($M\text{-}H_2Br_2$; 13%).

Pentane then eluted the monobromide XII, which on crystallization from pentane gave crystals (6·61 g, 64%), m.p. 48–52°, raised to m.p. 56–56·5° by sublimation at 55° (bath temp; 0·03 mm). (Found: C, 65·2; H, 3·85; Br, 31·8. $C_{14}H_9Br$ requires: C, 65·4; H, 3·55; Br, 31·1%); ν_{max} 3290, 3050, 2370, 1595, 945, 850, 822, 785, 775 and 750 cm^{-1}; λ_{max} 233 mμ (log ε 4·72) and 311 (4·07); NMR spectrum (CCl_4), 1H doublet (J = 14 c/s) at τ 1·49 (α-vinylic proton), 6H multiplet at τ 2·14–2·76 (aromatic protons), 1H doublet (J = 14 c/s) at τ 3·53 (β-vinylic proton)[17] and 1H singlet at τ 6·50 (acetylenic proton); mass spectrum, peaks at *m/e* 258, 256 (M^+; 26% each), 178 (M-Br + H; 24%), 177 (M-Br; 100%) and 176 (M-HBr; 56%). The substance was unstable, and was stored at −15°.

Hydrogenation of VI *and* IX *to 1,8-diethylnaphthalene* (X) *and 1,8-diethyltetralin* (XI)

The diene VI (200 mg) in EtOAc (50 ml) was shaken in H_2 over a pre-reduced Pt catalyst (ca. 100 mg) for 2 hr at room temp and atmospheric press. The catalyst was removed, the solvent was evaporated, and the residue (two spots on TLC) was chromatographed on Al_2O_3 (50 g, Camag activity I).

Pentane eluted firstly XI (40 mg, 19%) as a liquid; NMR spectrum (CCl_4), 3H multiplet at τ 2·8–3·2 (aromatic protons), 5H multiplet at τ 7·0–7·6 (benzylic protons), 6H multiplet at τ 7·8–8·5 (non-benzylic CH_2 protons) and 6H multiplet at τ 8·6–9·1 (CH_3 protons); mass spectrum, peaks at *m/e* 188 (M^+; 17%), 186 ($M\text{-}H_2$; 9%), 184 ($M\text{-}H_4$; 10%) and 159 ($M\text{-}C_2H_5$; 100%).

Pentane then eluted X (158 mg, 77%) as a liquid, which was distilled at 65° (bath temp, 0·3 mm). (Found: C, 91·5; H, 9·05. $C_{14}H_{16}$ requires: C, 91·25; H, 8·75%); $\nu_{max}^{CCl_4}$ 3055, 3035, 2965, 2925, 2870, 2850 and 826 cm^{-1}; $\lambda_{max}^{Et_2O}$ 277 mμ (log ε 3·84), 286 (3·91), 297 sh (3·75), 318 (2·75) and 322 (2·71); NMR spectrum (CCl_4), 6H multiplet at τ 2·18–2·70 (aromatic protons), 4H quartet (J = 7 c/s) at τ 6·80 (CH_2 protons) and 6H triplet (J = 7·5 c/s) at τ 8·72 (CH_3 protons); mass spectrum, peaks at *m/e* 184 (M^+; 98%), 169 ($M\text{-}CH_3$; 100%), 155 ($M\text{-}C_2H_5$; 57%), 154 ($M\text{-}C_2H_6$; 30%), 153 ($M\text{-}C_2H_7$; 28%) and 152 ($M\text{-}C_2H_8$; 24%).

Catalytic hydrogenation of the diyne IX under the same conditions gave essentially the same result, 24% of XI and 73% of X being obtained.

Oxidative coupling of IX *to cyclic dimer* XX

(a) *Cuprous chloride method.* CuCl (10 g), NH_4Cl (32 g), H_2O (85 ml) and conc HClaq (0·2 ml) were stirred at 45–50° in a flask fitted with a reflux condenser and a gas inlet tube. A soln of IX (500 mg) in EtOH (25 ml) was added, followed after 1 min by EtOH (15 ml) and benzene (100 ml). A vigorous stream of O_2 was passed into the well-stirred mixture, which was kept at 45–50°. The reaction was allowed to proceed at this temp for 30 min, the volume being maintained by periodic addition of benzene. The mixture was cooled, and the dark brown benzene layer was separated. The green aqueous layer was diluted with 2N HCl and extracted with benzene. The combined benzene extracts were washed with 2N HCl and H_2O. The benzene soln was then shaken with a soln of $AgNO_3$ (10 g) in 95% EtOH (200 ml) for 5 min, the mixture was allowed to stand for 15 min, and the brown ppt was removed. The filtrate was washed well with H_2O, dried and evaporated under reduced press (bath temp below 30°) to ca. 50 ml. The dark brown soln was chromatographed on Al_2O_3 (200 g, Camag activity I). Pentane–ether (7:3) eluted XX in 12 successive pink fractions (50 ml each); all showed the same UV spectra and were homogeneous by TLC. Each fraction was diluted with ether (50 ml) and evaporated to ca. 20 ml. The combined red-pink fractions showed λ_{max} 328 mμ (log ε 4·00), 502 (3·46) and 540 (3·67) (see Fig. 1).* For storage, the original chromatography fractions were diluted with EtOAc, and such solns could be kept with only little decomposition for 1–2 days at −15°. All attempts to prepare concentrated $CHCl_3$ or CCl_4 solns for determination of NMR and IR spectra resulted in a brown polymer. Attempted determination of the mass spectrum also resulted in decomposition. The yield of XX was estimated to be ca. 11 mg (2·2%), from the hydrogenation results (see below).

(b) *Cupric acetate method.* A soln of IX (500 mg) in pyridine (10 ml) and MeOH (10 ml) was added to $Cu(OAc)_2 \cdot H_2O$ (3 g) in pyridine (25 ml) and MeOH (25 ml). The mixture was stirred, introduced into an oil bath at 100–110°, and allowed to boil under reflux for 10 min. The cooled mixture was poured into benzene (250 ml) and 3N HCl (250 ml). The benzene layer was washed with H_2O, and then with $AgNO_3$aq, as described under (a). The ppt was removed, the filtrate was washed with H_2O, dried and evaporated under reduced press (bath temp below 30°) to ca. 20 ml. The dark brown soln was chromatographed on Al_2O_3 (300 g, Camag activity II). Pentane–ether (9:1) eluted the cyclic dimer XX in pink fractions, showing UV spectra identical with the previously described material. The yield (estimated spectroscopically) was 0·8 mg (0·16%). The yield of XX was even lower when the cupric acetate oxidation was carried out under other conditions.

Hydrogenation of cyclic dimer XX

The fractions containing XX (obtained by oxidation of 500 mg IX by the CuCl method, see (a) above) were diluted with EtOAc (240 ml), evaporated to ca. 100 ml under reduced press, and the red soln was shaken in H_2 over a pre-reduced Pt catalyst (ca. 100 mg) for 2 hr at room temp and atm press. Removal of the catalyst and evaporation of the solvent then yielded a yellow liquid residue (11 mg).

The hydrogenation products from 5 separate coupling experiments (each from 500 mg IX) were combined, and subjected to thick layer chromatography on Kieselgel $HF_{254+366}$. Three separate bands were obtained (in about equal quantities), labelled 1, 2 and 3 in order of elution (pentane).

Band 1 consisted of a liquid, assigned the naphthalene–tetralin structure XXI; $\lambda_{max}^{Et_2O}$ 270 mμ (rel int 0·86), 280 (1·00), 290 (0·79), 296 sh (0·60), 305 (0·35), 310 (0·32) and 323 (0·19); mass spectrum, peaks at *m/e* 368 (M^+; 95%), 366 ($M-H_2$; 65%), 364 ($M-H_4$; 70%), 362 ($M-H_6$; 100%) and 360 ($M-H_8$; 40%).

Band 2 consisted of a liquid, assigned the dinaphthalene structure XXII; $\lambda_{max}^{Et_2O}$ 276 mμ (rel int 0·95), 287 (1·00) 295 sh (0·93) and 324 (0·44); mass spectrum, peaks at *m/e* 364 (M^+; 80%), 362 ($M-H_2$; 100%), 360 ($M-H_4$; 43%) and 358 ($M-H_6$; 21%).

Band 3 consisted of a liquid, assigned a hexacyclic dinaphthalene structure (e.g. XXIII); $\lambda_{max}^{Et_2O}$ 270 mμ (rel int 0·85), 280 (1·00), 290 sh (0·83), 296 (0·61), 305 (0·38), 310 (0·37) and 323 (0·24); mass spectrum, peaks at *m/e* 362 (M^+; 100%) and 360 ($M-H_2$; 70%.)

Oxidative coupling of XII *to* XXIV

A mixture of XII (500 mg), $Cu(OAc)_2 \cdot H_2O$ (10 g) and pyridine (100 ml) was stirred at 55° for 3 hr. The product was isolated with benzene and chromatographed on Al_2O_3 (100 g, Camag activity I). Pentane–ether (19:1) eluted firstly unchanged XII (20 mg), followed by XXIV (5 mg, 1%), yellow oil, homogeneous by TLC; longest wave-length max at 430 mμ; mass spectrum, peaks at *m/e* 514, 512, 510 (M^+; 7·5, 15, 7·5%), 432, 430 ($M-HBr$; 7% each), 431, 429 ($M-H_2Br$; 21% each), 422, 420 ($M-CBr + H$; 33%), 350 ($M-2HBr$; 16%) and 178 ($M-C_{14}H_6Br_2$; 100%).

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* See footnote ‡, page 1399.

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REFERENCES

[1] For Part LI, see A. Shani and F. Sondheimer, *J. Am. Chem. Soc.* in the press.

[2] Present address: Chemistry Department, University College, London W.C.1.

[3] Method of R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.* **74**, 1406 (1952).

[4] See G. Ghilardi and G. Kalopissis, *Bull. Soc. Chim. Fr.* 217 (1952).

[5] E. D. Bergmann and J. Szmuszkovicz, *J. Am. Chem. Soc.* **75**, 2760 (1953).

[6] E. D. Bergmann and I. Agranat, *J. Org. Chem.* **31**, 2407 (1966).

[7] H. J. Bestmann, H. Haberlein, H. Wagner and O. Kratzer, *Chem. Ber.* **99**, 2848 (1966).

[8] J. K. Stille and R. T. Foster, *J. Org. Chem.* **28**, 2703 (1963).

[9] See O. M. Behr, G. Eglinton, A. R. Galbraith and R. A. Raphael, *J. Chem. Soc.* 3614 (1960).

[10] H. A. Staab and F. Graf, *Tetrahedron Letters* 751 (1966).

[11] S. Akiyama, S. Misumi and M. Nakagawa, *Bull. Chem. Soc. Japan* **33**, 1293 (1960).

[12] For reviews, see G. Eglinton and W. McCrae, *Advances in Organic Chemistry, Methods and Results* (Edited by R. A. Raphael, E. C. Taylor and H. Wynberg) Vol IV, pp. 225–328. Interscience, New York (1963); F. Sondheimer, *Pure Appl. Chem.* **7**, 363 (1963); *Proc. Roy. Soc. A* **297**, 173 (1967).

[13] R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.* **87**, 5720 (1965).

[14] S. Akiyama, S. Misumi and M. Nakagawa, *Bull. Chem. Soc. Japan* **35**, 1829 (1962); G. Eglinton and W. McRae, Ref. 12.

[15] A. I. Vogel, *Practical Organic Chemistry* (3rd Edition) p. 252. Longmans, London (1961).

[16] For the NMR spectrum of the related αβ-dibromoethylbenzene, see *NMR Spectra Catalog* Vol. 2; Spectrum No. 503. Varian Associates (1963).

[17] For the NMR spectrum of the related *trans*-β-bromostyrene, see *NMR Spectra Catalog*, Vol. 2; Spectrum No. 497. Varian Associates (1963).