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# THE REACTION OF 1,8-BIS(TRIPHENYLPHOSPHONIOMETHYL)NAPHTHALENE DIBROMIDE WITH 2,2'-BIPHENYLDICARBOXALDEHYDE AND o-PHTHALALDEHYDE. TRANSANNULAR REACTIONS IN THE 11- AND THE 9-MEMBERED RING SERIES (1)

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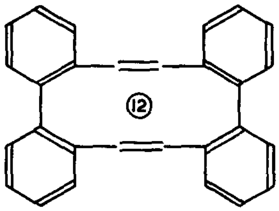
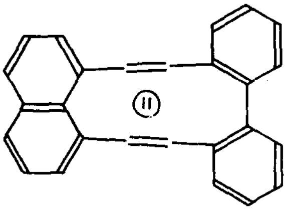
We have reported recently that the Wittig reaction between the bis-ylid derived from 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide (VII) and 1,8-naphthalenedicarboxaldehyde gives rise to the 10-membered ring compound IV (4). The possibility existed that the analogous reaction of this bis-ylid with 2,2'-biphenyldicarboxaldehyde (VIII) would lead to the 11-membered ring compound II, while reaction with o-phthalaldehyde (XVI) would yield the 9-membered ring compound V. It was of interest to investigate the transannular reactions of II



I



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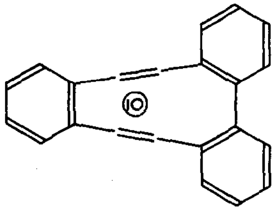

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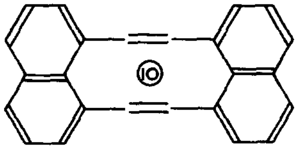

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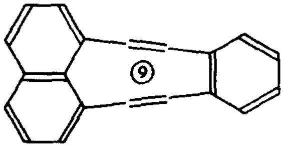

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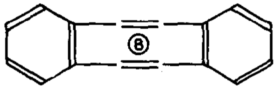


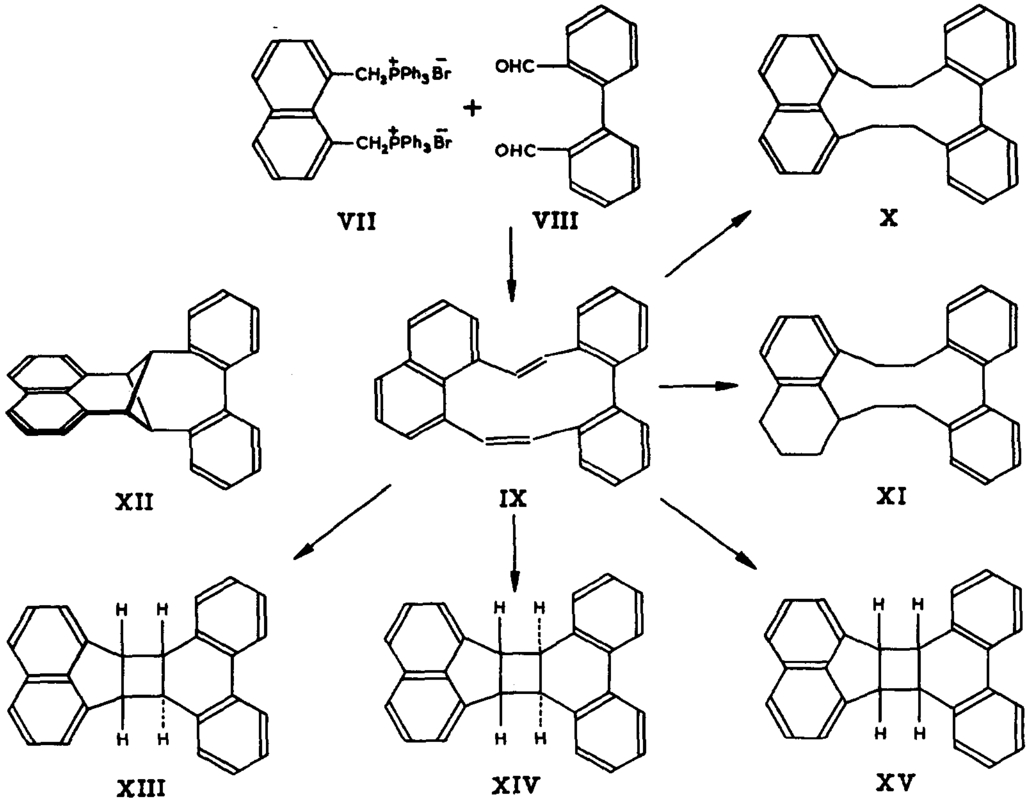
VI

and V, and to compare their properties to those of the related I (5, 6), III (7), IV (4), and VI (8).

The Wittig reaction between the bis-ylid derived from VII (9) and VIII (10) was studied under different conditions. The best results were obtained when equimolar amounts of VII and VIII in methanol were added slowly to a solution of lithium methoxide in methanol at room temperature. This procedure gave IX (= *cis*-*trans*-II) in 58% yield as colourless needles (11), mp 143-144°; mass spectrum, mol. ion *m*/*e* 330.140 (calcd. 330.141); uv (determined rapidly), $\lambda_{max}^{Et_2O}$ 228 mμ (log ε 4.81), 293sh (3.91), 306sh (3.97), and 322 (4.00); ir (all in KBr), band at 986(m) $cm^{-1}$ (*trans* double bond); nmr (all at 100 Mcps) ($CCl_4$), τ 2.2-3.0 (m, 15, aromatic + 1 olefinic H), 3.46 (d, 1, *J* = 12.5 Hz, olefinic H), 3.77 (d, 1, *J* = 12.5 Hz, olefinic H), and 4.08 (d, 1, *J* = 16.5 Hz, olefinic H). The *cis*-*trans* configuration is based on the ir and nmr spectra.

Catalytic hydrogenation of IX in ethyl acetate over 5% Pd - $CaCO_3$ for 30 min gave 52% of the naphthalene derivative X and 29% of the tetralin derivative XI. Substance X showed mp 154-155°; mass spectrum, mol. ion *m*/*e* 334.173 (calcd. 334.172); uv, $\lambda_{max}^{C_6H_{12}}$ 231 mμ (log ε 4.78), 281 (3.86), 292 (3.96), 302 (3.81), 320 (2.93), and 324 (2.84); ir, no band at *ca* 986 $cm^{-1}$; nmr ($CCl_4$), τ 2.4-3.3 (m, 14, aromatic H) and 6.1-7.7 (m, 8, methylene H). Substance XI exhibited mp 138-140°; mass spectrum, mol. ion *m*/*e* 338.202 (calcd. 338.203); uv, $\lambda_{max}^{C_6H_{12}}$ 264 mμ (log ε 3.10) and 273 (2.96); nmr ($CCl_4$), τ 2.7-3.5 (m, 11, aromatic H) and 6.5-8.9 (m, 15, aliphatic H).

A new substance was formed rapidly when dilute solutions of IX were allowed to stand in light, or when the uv spectrum was determined; *e.g.*, *ca* 90% had been destroyed when a solution of IX (1 mg) in cyclohexane (50 ml) was allowed to stand in diffuse daylight for 50 min. The new substance, isolated in 72% yield by direct crystallization from a dilute cyclohexane solution after 1 day, formed colourless crystals, mp 190-191°; mass spectrum, mol. ion *m*/*e* 330.140; uv, $\lambda_{max}^{C_6H_{12}}$ 218 mμ (log ε 4.83), 224 (4.85), 231 (4.95), 271 (4.23), 278 (4.22), 290sh (4.12), 294 (4.15), 302 (4.03), 307 (3.88), 316 (3.11), and 321 (2.87); ir, no significant band at *ca* 986 $cm^{-1}$; nmr ($CCl_4$), τ 2.3-3.2 (m, 14, aromatic H), 5.3-5.7 (m, 2, cyclobutane H), 6.2-6.6 (m, 1, cyclobutane H) and 6.9-7.3 (m, 1, cyclobutane H). Attempted catalytic hydrogenation as above resulted in no change. The data show the substance to be a cyclobutane derivative. The complexity of the cyclobutane resonances in the nmr spectrum appears to rule out symmetrical

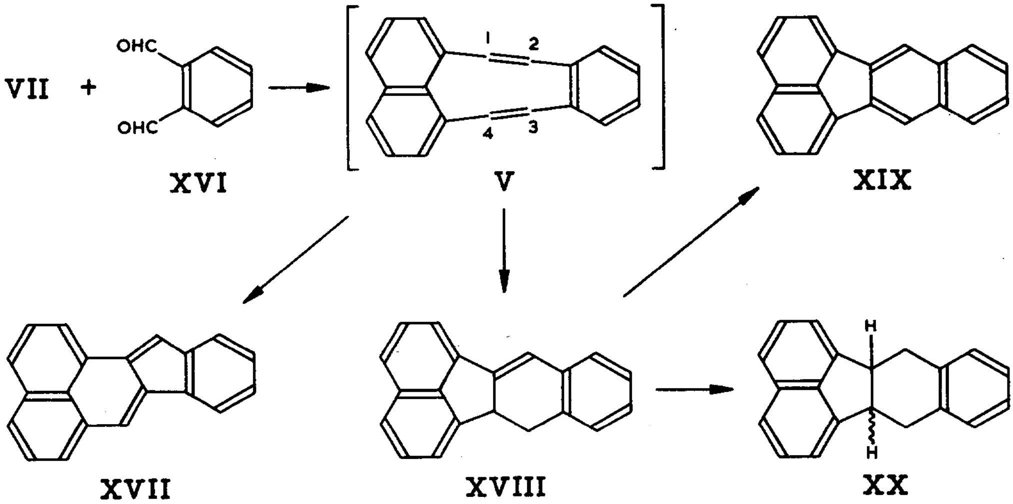


structures such as XII, XIV, and XV, and we tentatively assign structure XIII to the compound (containing a cyclobutane trans-fused to a six-membered ring). An X-ray crystallographic analysis is now being carried out in order to obtain definite structural information.

Pyrolysis of IX at 200° for 15 min yielded 45% of the "trans" cyclobutane XIV and 20% of the "cis" cyclobutane XV. Compound XIV formed colourless crystals, mp 291-292°; mass spectrum, mol. ion m/e 330.140; uv, $\lambda_{max}^{Et_2O}$ 220sh m$\mu$ (log $\epsilon$ 4.70), 231 (4.76), 254sh (3.89), 279sh (4.07), 284 (4.11), 292sh (4.06), 296 (4.05), 304sh (3.90), 310 (3.83), 312 (3.83), and 322 (3.20); ir, no band at ca 986 cm$^{-1}$; nmr ($AsCl_3$) (12), $\tau$ 1.9-2.9 (m, 14, aromatic H) and 6.10 ($A_2B_2$, 4, cyclobutane H). Compound XV was obtained as colourless crystals, mp 220-221°; mass spectrum, mol. ion m/e 330.140; uv, $\lambda_{max}^{Et_2O}$ 217 m$\mu$ (log $\epsilon$ 4.85), 277sh (4.11), 283 (4.14), 310 (3.78), 314 (3.80), and 323 (3.12); ir, no band at *ca* 986 $cm^{-1}$; nmr ($CD_2Cl_2$), $\tau$ 2.6-3.4 (m, 14, aromatic H) and 5.39 ($A_2B_2$, 4, cyclobutane H). The stereochemical assignments XIV and XV are based on the correspondence of the cyclobutane proton chemical shifts in the nmr spectra to those of the related "*trans*" and "*cis*" bis-naphthalene analogues ($\tau$ 6.00 and 5.30, respectively, in $CD_2Cl_2$) (4). Structure XII instead of XIV cannot be ruled out definitely for the substance of mp 291-292° (cyclobutane proton chemical shift in related bis-naphthalene analogue, $\tau$ 6.48 in $CD_2Cl_2$) (4), although it appears less probable on the basis of the mass and the uv spectra.

The pyrolysis of IX also gave acenaphthylene and phenanthrene, each in *ca* 10% yield, formed presumably via XIV and/or XV. The pyrolysis of the 11-membered ring compound IX (= *cis*-*trans*-II) resembles that of the 12-membered ring compound *trans*-*trans*-I (5) (which gives a cyclobutane derivative analogous to XIV or XV and then phenanthrene) rather than that of the 10-membered ring compounds *cis*-*trans*-III (7) and *cis*-*cis*-IV (4) (which give compounds containing only one additional bond).

Wittig reaction between VII and *o*-phthalaldehyde (XVI) under the same conditions used with VIII did not lead to V, but gave 16% of the known indeno[2,1-*a*]phenalene ("indeno[2,1-*a*]-perinaphthene") (XVII) (dark red crystals, mp 213-214°) (13) and 15% of the dihydro-benzo[*k*]-



fluoranthene XVIII. Substance XVIII formed colourless crystals, mp 134-135°; mass spectrum, mol. ion m/e 254.110 (calcd. 254.110); uv, $\lambda_{max}^{C_6H_{12}}$ 247 mμ (log ε 4.45), 252 (4.46), 274 (3.91), 284 (3.85), 321sh (4.02), 335 (4.28), 353 (4.45), and 372 (4.42); nmr ($CCl_4$), τ 2.4-3.2 (m, 11, aromatic + 1 olefinic H), 5.88 (dd, 1, *J* = 15, 6 Hz, methine H), 6.72 (dd, 1, *J* = 15, 6 Hz, methylene H), and 7.18 (coincident dd, 1, *J* = 15, 15 Hz, methylene H). The structure of XVIII was supported by its ready dehydrogenation to the known benzo[k]fluoranthene (XIX) (colourless crystals, mp 217-218°) (14) by treatment with bromine in $CCl_4$ (78% yield), by pyrolysis at 200° for 2 hr (83% yield), or merely by allowing an unstoppered ether solution to stand for 2 days (75% yield). Catalytic hydrogenation of XVIII in ethyl acetate over 5% Pd-C gave 16% of XIX and 72% of the dihydro-compound XX, mp 158-159°; mass spectrum, mol. ion m/e 256.124 (calcd. 256.125); uv, $\lambda_{max}^{C_6H_{12}}$ 224 mμ (log ε 4.74), 230 (4.83), 246 (3.33), 259sh (3.43), 271 (3.70), 280 (3.87), 291 (3.93), 302 (3.75), 307 (3.60), 317 (3.07), and 321 (3.17); nmr ($CD_2Cl_2$), τ 2.4-3.1 (m, 10, aromatic H), 5.9-6.2 (m, 2, methine H), 6.6-6.9 (m, 2, methylene H), and 7.0-7.4 (m, 2, methylene H).

The above-described reaction of VII with XVI presumably first yields the 9-membered ring compound V. Bond formation between $C^1$-$C^3$ and hydrogen shift then gives a dihydro-derivative of XVII (which undergoes dehydrogenation to XVII), while bond formation between $C^1$-$C^4$ and hydrogen shift leads to XVIII. These transannular reactions resemble those observed with *cis-cis*-IV (4) and *cis-trans*-III (7), respectively. It is probable that XVII and XVIII are derived from different stereoisomers of V. This is suggested by the fact that the reaction (boiling benzene-ether, 3 hr) between XVI and the bis-ylid prepared from VII by treatment with sodamide (9) gave 7.5% of XVIII, but no XVII; presumably only one isomer of V is formed initially in this case.

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2. Recipient of a Science Research Council Research Studentship.

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6. The *cis*-*cis* isomer of I has been obtained in this Laboratory by the Wittig reaction of 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide with 2,2'-biphenyldicarboxaldehyde (VIII) (K. Grohmann, R.H. Mitchell, and F. Sondheimer, unpublished results; *cf.* E.D. Bergmann, *Bull.Soc.Chim.France* 2681 (1965)).

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