

SOME UNUSUAL HYDROCARBONS DERIVED FROM NAPHTHALENE

P.R. Houlton and W. Kemp

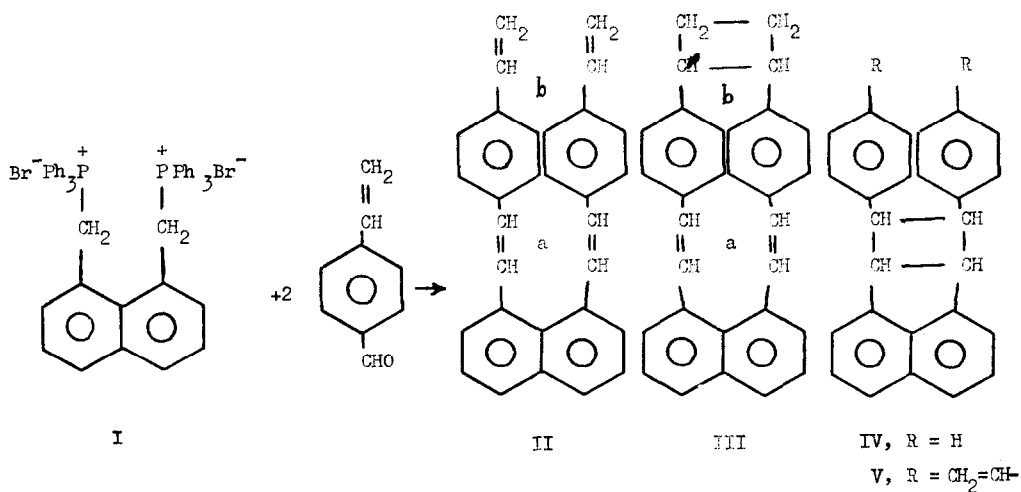
Department of Chemistry, Heriot-Watt University,
Edinburgh.

(Received in UK 21 May 1968; accepted for publication 24 June 1968)

Recently (1) we reported the formation of an unusual ring system in a synthetic sequence starting from (1,8-naphthylenedimethylene)bis-(triphenylphosphonium bromide), I. Further reactions in this series have been examined and shown to lead to unexpected products. Other synthetic routes to similar hydrocarbons are also discussed.

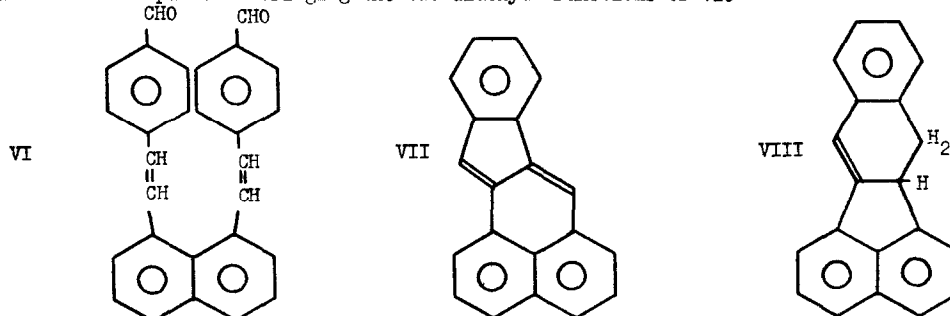
The Wittig reaction between I and 4-formylstyrene under the conditions specified previously (1) leads expectedly to yellow plates (50%) of II, 1,8-bis(4'-vinylstyryl)naphthalene; m.p. (from benzene/ethanol) 180°. Calculated for C₃₀H₂₄, C, 93.75; H, 6.25. Found C, 93.48; H, 5.99%. λ_{\max} (EtOH), 215 m μ (log ϵ 4.47), 248 m μ (4.32), 280 m μ (4.48), 350 m μ (4.32) $\tau_{\text{ar} + \text{CH}_a}$ 1.9-3.1, τ_{CH_b} 3.25-3.55, τ_{CH_2} 4.2-4.9.

Irradiation of II in boiling cyclohexane with 253.7 m μ light gave colourless cubes (92%) of 1,8-4',4''-(1,2-cyclobutano)styryl naphthalene, III. m.p. (from D.M.F.) 295° dec. Calculated for C₃₀H₂₄, C, 93.75; H, 6.25. Found C, 93.42; H, 6.21%. λ_{\max} (EtOH), 210 m μ (log ϵ 4.18), 248 m μ (4.30), 265 m μ (4.18), 350 m μ (4.00). $\tau_{\text{ar} + \text{CH}_a}$ 2.05-3.4, τ_{CH_b} 5.62, τ_{CH_2} 7.4.



The structure of this remarkable 17-membered ring system is established both from the n.m.r. evidence and, especially, from its ultraviolet absorption spectrum; this is very similar to that of the starting material, II, and of 1,8-distyrylnaphthalene. Irradiation of 1,8-distyrylnaphthalene produces IV (1), but had irradiation of II produced V, then we should have expected a spectrum more akin to that of II, which has one principal absorption at 225 μ . The n.m.r. spectrum of the product is wholly consistent with the structure III, and not at all with V.

The reaction between I and terephthalaldehyde gave green-fluorescent plates (25%) of 1,8-bis(4-formylstyryl)naphthalene, VI. m.p. (from benzene) 222°. Calculated for $C_{28}H_{20}O_2$, C, 86.60; H, 5.25. Found C, 86.62; H, 5.40%. λ_{\max} (EtOH), 224 μ (log ϵ 4.60), 287 μ (4.53), 357 μ (4.50). τ_{ar} 1.7-2.5, τ_{CH} 2.6-3.1, τ_{CHO} 0.0 $\nu_{\text{C=O}}$ (KBr) 1715 cm^{-1} . We were unable to induce further reaction between VI and I; for steric reasons, one molecule of I will be incapable of bridging the two aldehyde functions of VI.

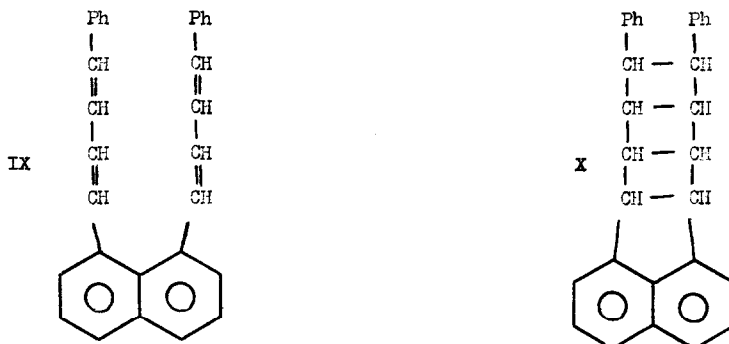


The reaction between I and isophthalaldehyde produces 5% of hydrocarbon material, m.p. (from benzene/petrol, 40-60°) 156°. λ_{\max} (EtOH), 225 μ , 248 μ , 340 μ . $\tau_{\text{ar}} + \text{CH}$ 2.1-3.4. Analysis indicates $C_{30}H_{22}$, but we are unable to accommodate all these data in any one structure.

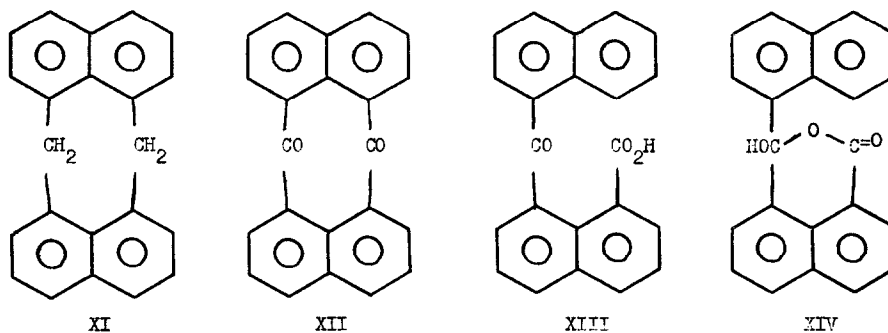
The reaction between I and phthalaldehyde we found to give VII and VIII, confirming the report of Mitchell and Sondheimer (2), but we isolated these compounds in 25% and 10% yield respectively. We have also carried out dehydrogenation and bromination of VIII and our results agree with those of Mitchell and Sondheimer.

The reaction between I and cinnamaldehyde gave colourless plates (42%) of 1,8-bis(4-phenylbuta-1,3-dienyl)naphthalene, IX. m.p. (from benzene) 165°. Calculated for $C_{30}H_{24}$, C, 93.75; H, 6.25. Found, C, 93.86; H, 6.12%. λ_{\max} (EtOH), 225 μ (log ϵ 4.39), 251 μ (4.39), 282 μ (4.48), 353 μ (4.35). Fluorescence spectrum 465 μ (broad band). τ_{ar} 2.1-2.8, τ_{CH} 2.9-3.1 Irradiation of IX in boiling tetrahydrofuran with 253.7 μ light

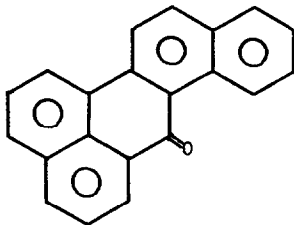
produced a number of compounds which have defied all attempts to separate them. From spectroscopic evidence the irradiation product is completely cross-bonded as in X, but this structure represents a number of stereoisomers.



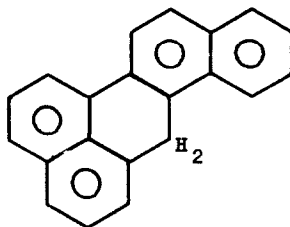
In an effort to produce a hydrocarbon with an eight-membered ring system, we turned our attention to the synthesis of 1,8-(1',8'-naphthalylidimethyl)-naphthalene, XI, (3). Knapp (4) reported the synthesis of 1,8-naphthaloylnaphthalene, XII, by phosphorus pentoxide cyclization of the readily available 8-(1'-naphthyl)-1-naphthoic acid, XIII. We have repeated this work and found that the naphthoynaphthoic acid exists as the lactol XIV. ν_{OH} (KBr) 3300 cm^{-1} , $\nu_{C=O}$ one sharp peak at 1690 cm^{-1} . Cyclization of the lactol does not produce XII, but a complex mixture of ketonic material (5); thin layer chromatography showed no single major component. Direct reduction of the mixed ketones (zinc dust in fused zinc chloride-sodium chloride) produced two hydrocarbons of the phenalene series in very low yield, but no 1,8-(1',8'-naphthalylidimethyl)naphthalene, XI.



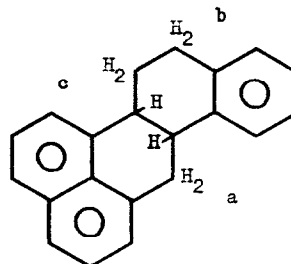
Clearly decarboxylation has caused loss of carbon, subsequent arylation in the 2-position leading to the naphthophenalone XV. The hydrocarbons isolated from the reduction by repeated chromatography on alumina are XVI and XVII.



XV



XVI



XVII

Compound XVI, 7,8-(1',2'-naphtho)phenalene: 5% overall from the mixed ketones; m.p. (from benzene/petrol, 40-60°) 210°. Calculated for $C_{21}H_{14}$, C, 94.74; H, 5.26. Found, C, 94.12; H, 5.02%. λ_{\max} (EtOH), 216 $m\mu$ (log ϵ 4.00), 261 $m\mu$ (4.46), 280 $m\mu$ (4.17), 289 $m\mu$ (3.85), 333 $m\mu$ (3.77). τ_{ar} 1.9-2.7, τ_{CH_2} 5.6.

Compound XVII, 7,8-[1',2'-(1',2',3',4'-tetrahydronaphtho)]phenalene: 2% overall from the mixed ketones; m.p. (from benzene) 155°. Calculated for $C_{21}H_{18}$, C, 93.34; H, 6.66. Found, C, 93.61; H, 7.09%. λ_{\max} (EtOH), 230 $m\mu$ (log ϵ 4.38), 266 $m\mu$ (4.81), 280 $m\mu$ (4.40), 289 $m\mu$ (4.15), 330 $m\mu$ (3.99). τ_{ar} 1.4-2.8, τ_{CH} 5.80. $\tau_{CH_2^a} + CH_2^b$ 6.85, $\tau_{CH_2^c}$ 7.9.

References.

1. P.R. Houlton and W. Kemp, Tetrahedron Letters, 1968, 9, 1045.
2. R.H. Mitchell and F. Sondheimer, ibid, 1968, 24, 2873.
3. P.R. Houlton and W. Kemp, J. Chem. Soc., 1967, 591. See also P.T. Lansbury and M. Klein, Tetrahedron Letters, 1968, 1961.
4. W. Knapp, Monatsh. Chem., 1936, 67, 332.
5. W.C. Agosta, J. Amer. Chem. Soc., 1967, 89, 3505.