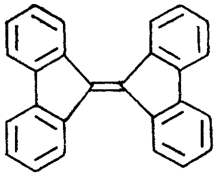
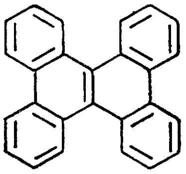
Rearrangement of Bifluorenylidene to Dibenzo[*g,p*]chrysene

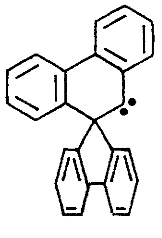
By **Roger W. Alder** * and **Graham Whittaker**, School of Chemistry, University of Britsol, Cantock's Close, Bristol BS8 1TS

In the vapour phase, at temperatures above 400°, bifluorenylidene (1) rearranges fairly cleanly to dibenzo[*g,p*]-chrysene (2). The reaction is accelerated in the presence of decomposing iodomethane and it is suggested that the mechanism involves a sequence of homoallyl–cyclopropylcarbinyl rearrangements occurring in adduct radicals. The reaction constitutes a simple preparative procedure for (2).

LANG *et al.*[1] have reported that thermolysis of fluorene at 700—750° gave rise to a number of polycyclic aromatic hydrocarbons. The major product was dibenzo[*g,p*]-chrysene (2), and it was suggested that this arose *via* bifluorenylidene (1). However this hypothesis was never substantiated by evidence that (1) was present in the products or that it could be rearranged to (2) under the conditions used. We were interested by this reaction in connection with our studies [2] of the rearrangement of azulene to naphthalene since it represented another example of thermal rearrangement of a non-benzenoid hydrocarbon to a benzenoid isomer.


(1)


(2)


(3)

RESULTS AND DISCUSSION

We have found that (1) does indeed rearrange to (2) even under conditions which are much milder than those originally used in the fluorene thermolysis. Thus (1) (10 mg), sealed in a 100 ml ampoule and heated for 3 h at 440° (conditions closely similar to those used in our studies [2] of azulene thermolysis), was almost completely converted into (2) with only trace amounts of unidentified orange contaminants.

Several mechanisms were initially considered for this rearrangement. Bifluorenylidene (1) is twisted due to steric overcrowding even in its ground vibrational state,[3] and it seemed possible that the perpendicular biradical from (1), easily available thermally, might be involved in a unimolecular rearrangement. Thus the biradical and the carbene (3) might not be very different in energy and (3) might be attainable by a 1,2-aryl shift. A further 1,2-aryl shift in (3) would give (2).

Another possibility was protonation of (1) by acidic sites on the glass surface of the ampoule to give the fluoren-9-ylfluoren-9-ylium cation which could then undergo well precedented 1,2-aryl shifts and proton loss to give (2). Even if this were not the mechanism under the thermolysis conditions, rearrangement *via* this route might occur under other conditions. However attempts to bring about rearrangement in polyphosphoric acid at temperatures up to 250° (2 h heating) gave products which did not appear to contain (2).

In view of our results with the azulene rearrangement [2] we considered the possibility that a similar mechanism operated in the present case involving a sequence of rearrangements in radical adducts (Scheme 1). If this mechanism were correct, rearrangement might be accelerated by providing an independent source of initiating radicals. Bifluorenylidene would probably not be fully vaporised at the temperatures (*ca.* 300°) used to generate methyl radicals from azomethane as in our azulene experiments.[2] It was desirable to work at *ca.* 400° and iodomethane (C–I bond strength *ca.* 225 kJ

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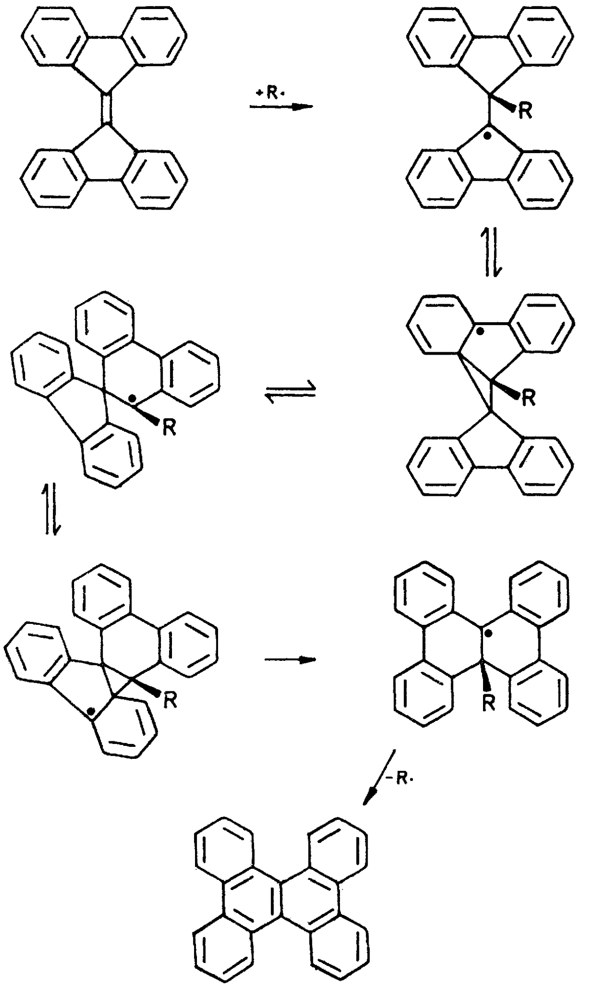
[1] K. F. Lang, H. Buffleb, and J. Kalowy, *Chem. Ber.*, 1961, **94**, 523.

[2] R. W. Alder and G. Whittaker, *J.C.S. Perkin II*, following paper.

[3] S. C. Nyburg, *Acta Cryst.*, 1954, **7**, 779.

mol^{-1}; known to yield CH_3 radicals[4]) seemed a convenient radical source. Thermolysis of (1) (10 mg) with iodomethane (*ca.* 0·7 mg) for 2 h at 400° gave >95% conversion to (2) (analysis by 100 MHz n.m.r.). In a control experiment (no CH_3I), rearrangement had only

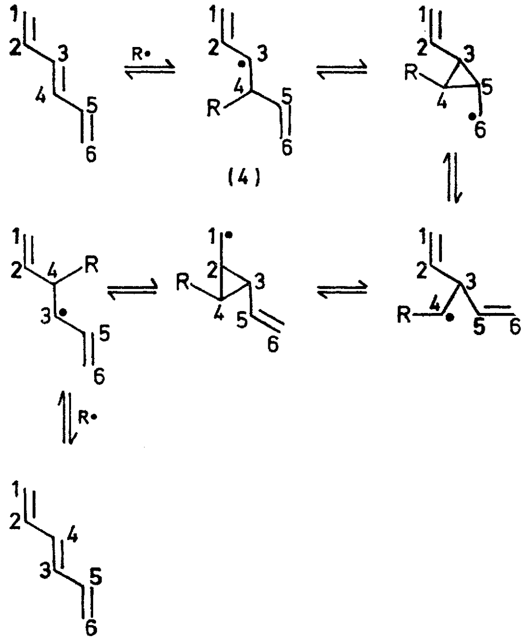


Scheme 1

occurred to the extent of 9%. Radical addition is known[5] to occur at the ethylenic bond of (1), and Scheme (1; R = Me) provides a simple and economical interpretation of the iodomethane result. In the absence of other evidence, we suggest that Scheme [1; R = H or some carbon radical derived from (1)] is a likely mechanism for the uncatalysed reaction.

Scheme 1 and our proposed mechanism for the azulene–naphthalene rearrangement are particular examples of a general rearrangement sequence, shown at its simplest in Scheme 2. This sequence does not seem to have been suggested before and in general it will have to compete with other pathways, *e.g.* radical addition at the termini of the hexatriene unit, cyclisation of a (*cis*-3,4-)hexatriene and of various intermediate radicals [though cyclopropane formation may well be the kinetically preferred path for (4) even when five-membered ring formation is possible], and finally, bimolecular hydrogen abstraction and other substitution pathways in (4) and other radicals.

Finally, in complete contrast to the azulene thermolysis, conversion of (1) into (2) is preparatively useful, since (1) is readily available from fluorene.



Scheme 2

EXPERIMENTAL

Bifluorenylidene was prepared from 9,9-dichlorofluorene as described by Schmidt and Wagner.[6] Dibenzo[*g,p*]-chrysene was isolated from a larger scale (40 mg) thermolysis of bifluorenylidene by extraction of the crude product with benzene and chromatography on alumina with 2 : 1 light petroleum–benzene eluant. The off-white crystalline fraction was recrystallised from light petroleum (b.p. 100—120°) to give dibenzo[*g,p*]chrysene, m.p. 214·5—215·5° (lit.,[7] 215°), *m/e* 328 (M^+) (Found: C, 95·2; H, 4·8. Calc. for $C_{26}H_{16}$: C, 95·1; H, 4·9%), τ[8] ($CDCl_3$) 1·35 (8H) and 2·40 (8H), $\lambda_{max.}$ (MeOH) 210 (log ε 4·78), 246 (4·48), 268 (4·68), 288 (4·67), 301 (4·83), 337 (4·19), 350 (4·17), and 383 (3·04). Bifluorenylidene and the dibenzochrysene could not be resolved by t.l.c. in any solvent system tried, though the latter could be detected in the combined spot by its intense fluorescence under u.v. irradiation. Mixtures of the two could be analysed by 100 MHz n.m.r.

Thermolyses were conducted as described in our paper on the azulene rearrangement.[2] Iodomethane was transferred to the ampoule on a vacuum line.

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[4] E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19; C. Horrex and R. Lapage, *Discuss. Faraday Soc.*, 1951, **10**, 233.

[5] M. Szwarc and J. H. Binks in 'Theoretical Organic Chemistry, I.U.P.A.C. Kekulé Symposium,' Butterworths, London, 1959, p. 262.

[6] J. Schmidt and H. Wagner, *Ber.*, 1910, **43**, 1796.

[7] E. Clar in 'Polycyclic Hydrocarbons,' Springer–Verlag, Berlin, 1964, vol. 1, p. 283.

[8] R. H. Martin, N. Defay, F. Geerts-Evrard, and S. Delavarene, *Bull. Soc. chim. belges*, 1964, **73**, 189.