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EPIMERIZATIONS OF PERHYDROPHENANTHRENES

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The problem of the configurations of the six epimeric perhydrophenanthrenes was dealt with by Linstead and coworkers in the classical series of papers published in 1942 and in 1950[1]. In these publications the stereochemistry of a few ketoperhydrophenanthrenes was correlated with that of perhydrodiphenic acids of known configurations. However the configurations and the relative stabilities of the perhydrophenanthrene hydrocarbons have not been established until very recently[2]. Conventional equilibration techniques could not be applied to these hydrocarbons since they cause extensive skeletal isomerizations[3].

We report here on the use of the previously described method for the equilibration at tertiary carbon atoms[4] for the assignment of configurations to these hydrocarbons.

A sample of perhydrophenanthrene obtained by hydrogenation of phenanthrene[5] over Raney nickel, which consisted of a mixture of the six epimers [labelled A to F according to their reciprocal retention times in glpc analysis (fig. 1a)][6], was irradiated with 254 nm light[7] in an evacuated tube, in cyclohexane solution and in the presence of an excess of mercuric bromide. After ca. 18 hr irradiation of this mixture of epimers, the glpc analysis revealed that the amounts of B and C increased while D,E, and F dissapeared, and that the amount of A was only slightly changed (fig. 1b)[8]. After additional irradiation (40 hr), however, analysis by the method showed a striking increase in A and a decrease of B and C (Fig. 1c).

Furthermore, irradiation of the pure epimer under identical conditions (fig. 2a) resulted in a mixture of B and C (fig. 2b), both of which, after continued irradiation, were almost completely converted into A (fig. 2c). We have also irradiated cyclohexane solutions of B and C in the presence of mercuric bromide and observed their slow conversion to A. On the other hand the epimer A did not change even after prolonged irradiation.

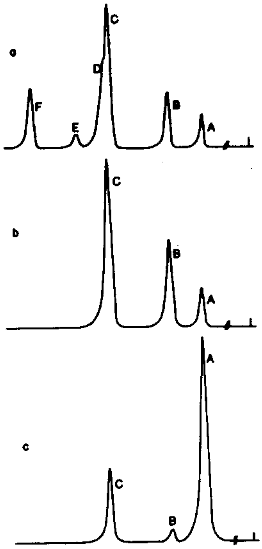


Fig. 1. Glp chromatogram of: (a) the mixture of six perhydrophenanthrenes obtained by hydrogenation of phenanthrene over Raney nickel; (b) the same mixture after 18 hr irradiation in the presence of $HgBr_2$; (c) the same mixture after 40 hr irradiation in the presence of $HgBr_2$.

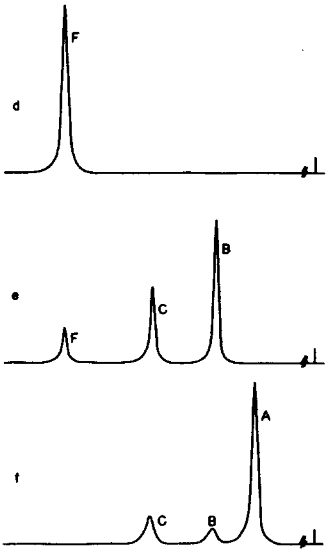
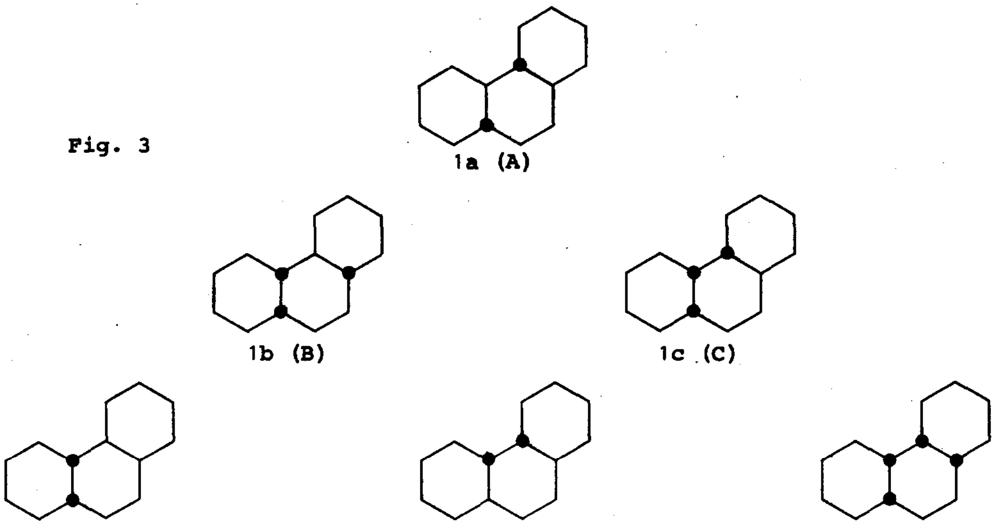


Fig. 2. Glp chromatogram of: (a) perhydrophenanthrene F; (b) epimer F after 5 hr irradiation in the presence of $HgBr_2$; (c) epimer F after 200 hr irradiation in the presence of $HgBr_2$.

These experiments clearly show that the six epimeric perhydrophenanthrenes can be arranged according to their relative stabilities in the following three groups. a) The least stable compounds D, E, and F; b) the more stable compounds B and C and c) the most stable epimer A.

It may be reasonably assumed that the most stable epimer A has the "all trans" configuration, 1a (fig. 3). Furthermore, since the epimerizations must occur in a stepwise manner through a series of inversions at a single tertiary carbon atom, each of D, E, and F can be assigned one of the structures 1d, 1e or 1f, and one of the structures 1b and 1c must thus belong to either B or C (fig. 3).

Fig. 3



1a (A)

1b (B)

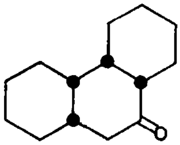
1c (C)

1d (D or E)

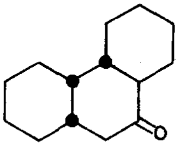
1e (D or E)

1f (F)

In order to decide between the alternative structures we have resorted to the results of Linstead and coworkers[1e]: Hydrogenation of 9-phenanthrol over platinum gave the "all-cis" 9-hydroxy-perhydrophenanthrene[9], which was oxidized to the 9-ketone 2a, the latter was then epimerized with acid to 2b[1e]. Clemmensen reduction of the ketone 2b resulted in the hydrocarbon 1c, while similar reduction of 2a gave a 2:1 mixture of 1f and 1c. The hydrocarbon 1f was found to be identical with F and 1c with C.



2a



2b

In this manner configurations were assigned to four of the epimers of perhydrophenanthrene, while the choice between 1d or 1e for D and E could not be determined.

The differences in free energy between any of the epimers belonging to the least stable group (1d, 1e or 1f) and any of the more stable ones (1b or 1c) should be greater then ca. 3 kcal/mol, since after a relatively short irradiation (before the formation of 1a) the proportion of the least stable epimers was <1%[10].

Similar energy differences probably exist between 1b or 1c and the most stable epimer 1a, although complete equilibration could not be reached in our experiments.

References

1) a. R.P. Linstead, W.E. Doering, S.B. Davis, P. Levine and R.R. Whetstone, *J. Amer. Chem. Soc.*, *64*, 1985 (1942); b. R.P. Linstead and W.E. Doering, *ibid.*, 1991, 2003 (1942); c. R.P. Linstead and S.B. Davis, *ibid.*, *64*, 2006, (1942); d. R.P. Linstead, S.B. Davis and R.R. Whetstone, *ibid.*, *64*, 2009 (1942); e. R.P. Linstead, R.R. Whetstone and P. Levine, *ibid.*, *64*, 2014 (1942); f. R.P. Linstaed and P. Levine, *ibid.*, *64*, 2022 (1942); g. R.P. Linstead, S.B. Davis and R.P. Levine, *J. Chem. Soc.*, 1425 (1950); h. R.P. Linstead and R.R. Whetstone, *ibid.*, 1428 (1950).

2) The only epimer of perhydrophenanthrene which has been previously fully characterised, mp 10°, [Beilstein E III, Vol. 5, 411 (1963)] has the "all-trans" configuration. *Cf.* R.P. Linstead and A.L. Walpole, *J. Chem. Soc.*, 842 (1939); *cf.* ref. 1h.

3) A. Scheneider, R.W. Warren and F.J. Janoski, *J. Org. Chem.*, *31*, 1617 (1966).

4) M. Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.*, *90*, 6540 (1960); M. Gorodetsky, D. Kogan and Y. Mazur, *92*, 1094 (1970).

5) J.R. Durland and H. Adkins, *J. Amer. Chem. Soc.*, *59*, 135 (1937).

6) For the glpc analyses a capilary column coated with propylene glycol (150 ft x 0.01 in) was used and for the glpc preparative separations a column of 10% carbowax on chromosorb W.A.W. (20 ft x 3/8 in).

7) The light source consisted of a set of five Philips TUV 15W germicidal lamps.

8) These are the absolute amounts which were deduced from the integrated values of the chromatogram's peaks with the aid of calibration curves of the pure isolated epimers.

9) The hydrocarbon fraction formed in this hydrogenation consisted of a 2:1 mixture of the epimers F and C.

10) For the calculations of the energy differences between the various epimers *cf*: W.S. Johnson, *J. Amer. Chem. Soc.*, *75*, 1498 (1953); E.L. Eliel "Stereochemistry of Carbon Compounds",Mc Graw & Hill Book Co. Inc., New York NY (1962) pp. 284-285; W.G. Dauben and K.S. Pitzer in M.S. Newman "Steric Effects in Organic Chemistry", John Wiley and Sons, New York, NY (1956) p. 31-35.