340. *Some Cyclodehydrogenation and Isomerisation Reactions of the Binaphthyls.*

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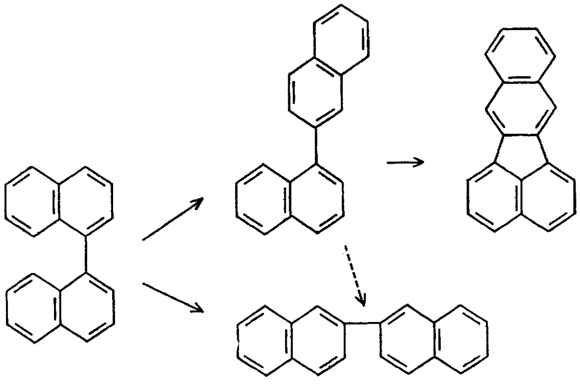
When 1,1′-binaphthyl is passed over platinum–alumina at 490° isomerisation is the main reaction, giving 1,2′- and 2,2′-binaphthyl. Some cyclodehydrogenation to benzo[*k*]fluoranthene also occurs. Cyclodehydrogenation predominates, however, when palladium–platinum–charcoal is used, but in this case perylene was the only product isolated. The three isomeric binaphthyls are interconvertible when passed over silica gel at 490°, the order of stability being 2,2′ > 1,2′ > 1,1′.

When perylene was required in this laboratory the most promising method for its preparation was by catalytic cyclodehydrogenation of 1,1′-binaphthyl, for which Orchin and Friedel[1] report an overall yield of 10% using a 30% palladium–charcoal catalyst mixed with asbestos and glass helices. It has now been found that using palladium–platinum–charcoal and a solution of 1,1′-binaphthyl in purified decalin gives a 40% yield (48% conversion) of perylene. When the decalin was omitted, most of the binaphthyl apparently carbonised and only a trace of perylene was formed. In an attempt to improve the yield further, a commercial platinum–alumina catalyst was tried. Chromatography and fractional crystallisation of the yellow product gave no perylene but, instead, 1,2′- and 2,2′-binaphthyl and benzo[*k*]fluoranthene. The relative amounts of these compounds suggest that the main reaction at 490° is direct isomerisation of 1,1′- to 2,2′-binaphthyl, perhaps through the 1,2′-isomer. The benzofluoranthene is probably formed by loss of hydrogen from 1,2′-binaphthyl as shown.



Orchin and Reggel[2] obtained benzo[*j*]- and benzo[*k*]-fluoranthene by passing 1,2′-binaphthyl over chromia–alumina at 500°. No benzo[*j*]fluoranthene was detected in our experiments.

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[1] Orchin and Friedel, *J. Amer. Chem. Soc.*, 1946, **68**, 573.

[2] Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.

In order to determine whether 2,2′-binaphthyl could be formed directly from the 1,2′-isomer the behaviour of the three isomers towards a recognised isomerisation catalyst (silica gel) was investigated: conversion of 1- into 2-phenylnaphthalene over silica gel at 350° had been reported.[3] The three binaphthyls were passed separately over silica gel at 490° and the products isolated by chromatography on activated alumina followed by fractional crystallisation. The yields of each isomer found in the products expressed as a percentage of the initial feedstock are summarised in the Table. Only very small amounts of 1,1′-binaphthyl were formed from the other two isomers, and the yields suggest that the order of stability at 490° is 2,2′ > 1,2′ > 1,1′-binaphthyl. Optimum conditions for these conversions have not been obtained.

	Yields (%)		
Binaphthyl	1,1′-	1,2′-	2,2′-
1,1′-	25·7	18·7	32·0
1,2′-	1·0	33·0	45·0
2,2′-	1·0	27·0	59·0

EXPERIMENTAL

Preparation of the Binaphthyls.—1,1′-Binaphthyl (m. p. 147·5°) was prepared in 57% yield by the reaction between 1-bromonaphthalene and copper powder.[4] Similarly, the reaction between 2-bromonaphthalene and copper powder gave the 2,2′-isomer (47%), m. p. 187°. 1,2′-Binaphthyl, m. p. 78°, was obtained in 48% yield by treating 1-tetralone with 2-naphthylmagnesium bromide.[5]

Apparatus.—The vessel consisted of a Pyrex-glass tube 30 in. long and of 0·5 in. internal diameter surrounded by an electrically heated steel tube. It was clamped vertically, and the operating temperature determined by means of an iron–constantan thermocouple placed between the tubes. The lower part of the glass tube contained the catalyst; the upper portion, packed with porcelain beads, acted as a preheater and vaporizer. A calibrated liquid-feed device, electrically wound, and controlled by a metal-in-glass valve, was fitted to the top of the tube, and an ice-cooled glass receiver connected to the bottom.

Attempted Cyclodehydrogenation of 1,1′-Binaphthyl over Platinum–Alumina.—A 0·6%, platinum on alumina catalyst (Catalyst R.D. 150; Baker Platinum Division, Engelhard Industries Ltd.) was used.

In a typical experiment, molten 1,1′-binaphthyl (8·55 g.) was passed over the catalyst (100 ml.) at 490° together with hydrogen (15 l./hr.) during 3 hr. Chromatography of the yellow product on activated alumina (P. Spence and Co. Type " H ", 100—200 mesh) gave colourless semisolid fractions on elution with light petroleum (b. p. 60—80°). Further chromatographing and fractional crystallisation gave unchanged 1,1′-binaphthyl (0·53 g.), m. p. 146°, mixed m. p. 146—147°, and 1,2′-binaphthyl (0·43 g.), m. p. and mixed m. p. 77°. Elution of the main column with gradually increasing amounts of benzene in light petroleum gave yellow fractions from which 2,2′-binaphthyl (1·13 g.), m. p. and mixed m. p. 187°, and benzo[*k*]fluoranthene (0·30 g.), m. p. and mixed m. p. 215°, were recovered. The identity of the last compound was confirmed by infrared examination. Elution of the main column with benzene gave more benzo[*k*]fluoranthene (0·30 g.).

Cyclodehydrogenation over Palladium–Platinum–Charcoal.—The preparation of the catalyst and purification of the decalin were carried out as previously described.[6] A solution of 1,1′-binaphthyl (5·25 g.) in decalin (26 ml.) was passed over the catalyst (70 ml.) at 490° during 3 hr. in hydrogen (7—8 l./hr.). Crystallisation of the product from benzene gave yellow-orange plates of perylene (0·94 g.), m. p. and mixed m. p. 274°. Removal of benzene, naphthalene, and decalin from the liquors by steam-distillation and chromatography of the dried residue on alumina gave unchanged 1,1′-binaphthyl (2·75 g.) and a further quantity of perylene (0·04 g.).

Silica-gel Isomerisations.—The catalyst was prepared by treating 1·45% acetic acid (2·4 l.) with sodium silicate (2 l.; s.g. 1·2 at 20°) and washing the resulting gel with water until it was

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[3] Mayer and Schiffner, *Ber.*, 1934, **67**, 67.
[4] Schoepfle, *J. Amer. Chem. Soc.*, 1923, **45**, 1566.
[5] Hooker and Fieser, *J. Amer. Chem. Soc.*, 1936, **58**, 1216.
[6] Baker, Warburton, and Breddy, *J.*, 1953, 4149.

free from sodium (flame test). Each of the binaphthyls was passed over the silica catalyst (60 ml. of 4—8 mesh) at 490° together with hydrogen (5—6 l./hr.). The products were separated and identified as previously described.

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