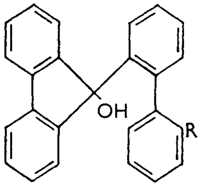
573. *The Alkaline Fusion of Biphenyl-2-carboxylic Acid. Pyrolysis of 2′-(9-Hydroxy-9-fluorenyl)biphenyl-2-carboxylic Acid.*

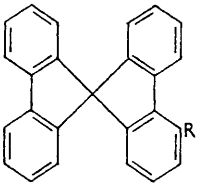
By D. H. Hey, J. A. Leonard, and C. W. Rees.

Kenner, Robinson, Tylor, and Webster[1] recently assigned structure (I) to the by-product obtained in the alkaline fusion of fluorenone and showed that, when heated, this by-product gave a mixture of 9,9′-spirobifluorene (II) and its 4-carboxylic acid (III). We had also obtained compounds (I),[2] (II), and (III) by the same reactions and our results, which largely support theirs, led us to the same structural conclusions.[3] Additional corroborating evidence, and certain minor differences from the results of the above workers, are described in the Experimental section.



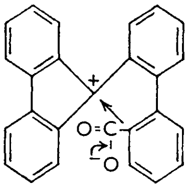
(I) R = CO_2H

(IV) R = H



(II) R = H

(III) R = CO_2H



(V)

Kenner *et al.* did not discuss the mechanism of the conversion of the hydroxy-acid (I) into a mixture of the spiran (II) and the spiran-acid (III). It is now shown that when the acid (I) is heated at 220°/2 mm. the spiran (II) and its acid (III) are formed in yields of 28% and 68%, respectively. This conversion is of interest for two reasons. First, the spiran-acid (III) was unchanged under these conditions and thus cannot be an intermediate in the formation of the spiran (II). Kenner *et al.*[1] did not record this, but did say that the acid (III) could be decarboxylated by heating it with soda-lime. Secondly, 2-(9-hydroxy-9-fluorenyl)biphenyl (IV), which lacks only the carboxylic acid group of compound (I), was also entirely unchanged when heated at 220°. The most obvious explanation for the second fact is that cyclodehydration of the hydroxy-acid (I) is intramolecularly acid-catalysed when heated alone at 220°. If this were so, cyclodehydration of the alcohol (IV) would probably be catalysed by aromatic carboxylic acids at this elevated temperature. This catalysis was demonstrated by heating a mixture of the, separately stable, alcohol (IV) and spiran-acid (III) at 220°: 9,9′-spirobifluorene (II) was formed. It is thus reasonable to view the direct conversion of the hydroxy-acid (I) into the spiran (II) as an electrophilic displacement of the carboxylate anion by the carbonium-ion centre (see V) derived from the zwitterionic form of (I). Such displacement will be faster than that of the un-ionised carboxylic acid group and can, apparently, compete effectively with displacement of a proton from the 6′-position. In the presence of strong acids substitution at the 6′-position, giving the spiran-acid (III), was the major reaction and only a small amount of the spiran (II) was formed. The dianion of the hydroxy-acid (I), which is formed at high temperature in its preparation from fluorenone, cannot give rise to the carbonium ion and is, therefore, thermally stable.

When the preparation of biphenyl-2-carboxylic acid from fluorenone and potassium hydroxide was extended by Huntress and Seikel[4] to certain chlorofluorenones anomalous, and unexplained, results were obtained. 1,8-Dichlorofluorenone (VI) gave the expected

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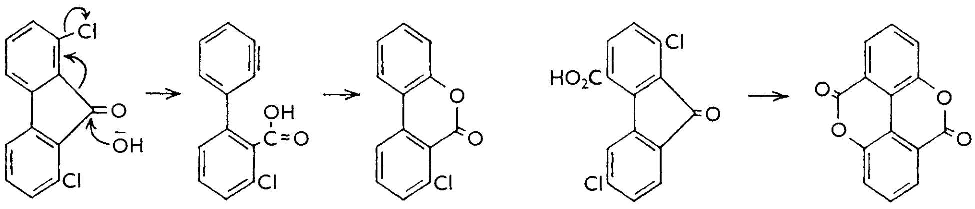
[1] Kenner, Robinson, Tylor, and Webster, *J.*, 1962, 1756.

[2] Hey, Leonard, and Rees, *J.*, 1962, 4579.

[3] Leonard, Ph.D. Thesis, London, 1962.

[4] Huntress and Seikel, *J. Amer. Chem. Soc.*, 1939, **61**, 1066, 1358.

3,3′-dichlorobiphenyl-2-carboxylic acid together with 6′-chloro-3,4-benzocoumarin (VIII) in 20—30% yield; and 1,6-dichlorofluorenone similarly gave 3′,5-dichlorobiphenyl-2-carboxylic acid and 4′-chloro-3,4-benzocoumarin (32%). 1,6-Dichlorofluorenone-4- (IX) and -5-carboxylic acid gave smaller yields of 6,6′-dihydroxydiphenic acid dilactone (X) and 4′-hydroxy-3,4-benzocoumarin-3′-carboxylic acid, respectively. Huntress and Seikel considered the anomalous reactions to proceed by replacement of the chlorine atom by a hydroxy-group followed by a rearrangement which, understandably, was not specified. Furthermore, they noted that this rearrangement occurred only when a chlorine atom was *ortho* to the carbonyl group; under the same reaction conditions 3,6-dichlorofluorenone, for example, simply gave 3′,5-dichlorobiphenyl-2-carboxylic acid. This fact, and the structures of the " abnormal " products may all be explained by the reasonable assumption that these reactions involve the formation of a benzyne intermediate (*e.g.*, VII), followed by intramolecular addition to it of the carboxylic acid group. Other examples of this type of reaction were reported recently.[5] Formation of the benzyne may well be concerted, as shown in (VI), since an intermediate aryl anion would probably be very rapidly protonated to give the " normal " reaction product, the biphenyl-2-carboxylic acid.



(VI) (VII) (VIII) (IX) (X)

Experimental.—Light petroleum refers to the fraction of b. p. 60—80°. Extracts were dried with anhydrous magnesium sulphate. Products were identified by mixed m. p. determination and by comparison of infrared spectra. 9,9′-Spirobifluorene (II), m. p. 206°, and 2-(9-hydroxy-9-fluorenyl)biphenyl (IV), m. p. 174°, were prepared according to directions of Clarkson and Gomberg [6] who record m. p.s 198—199° and 169—170°, respectively.

2′-(9-*Hydroxy*-9-*fluorenyl*)*biphenyl*-2-*carboxylic acid* (I). This acid, prepared as described before,[2] crystallised from benzene–light petroleum in colourless prisms, m. p. 181—182° (Found: C, 83·0; H, 5·1. Calc. for $C_{26}H_{18}O_3$: C, 82·5; H, 4·8%); its *benzylamine salt* separated quantitatively from benzene and had m. p. 209·5° (Found: C, 81·1; H, 5·7. $C_{33}H_{27}NO_3$ requires C, 81·6; H, 5·6%). The m. p. of the acid depended upon the rate of heating; at the m. p. it decomposed with gas evolution, resolidified, and then had m. p. 209—210°; it also decomposed slowly at 160°. The forms [1] of the acid with m. p.s 158° and 208—210° were not obtained. The infrared spectra of the acid in Nujol mull and in chloroform showed a strongly hydrogen-bonded hydroxyl and a carboxylic acid group.

Decomposition of the acid (I). (*a*) By heat. The acid (1 g.) was heated at 220°/2 mm. for 30 min. to give 9,9′-spirobifluorene (II) (0·24 g.), m. p. and mixed m. p. 206° [Found: C, 94·9; H, 5·0%; *M* (Rast), 344. Calc. for $C_{25}H_{16}$: C, 94·9; H, 5·1%; *M*, 316)], and 9,9′-spirobifluorene-4-carboxylic acid (III) (0·64 g.), m. p. 256° (231° after crystallisation from benzene–light petroleum) (Found: C, 86·6; H, 4·7%; *M*, 344. Calc. for $C_{26}H_{16}O_2$: C, 86·7; H, 4·5%; *M*, 360) [*benzylamine salt*, m. p. 197—199° (Found: C, 84·2; H, 5·6; N, 3·4. $C_{33}H_{25}NO_2$ requires C, 84·8; H, 5·4; N, 3·0%)], separated by sublimation, by chromatography on silica gel, or by extraction with hot dilute aqueous sodium hydroxide. Kenner *et al.*[1] report m. p. 197—198° and 223—224°, respectively, for compounds (II) and (III).

(*b*) By hydrochloric acid in acetic acid (cf. ref. 6). The acid (1 g.) in hot acetic acid (4 ml.) was treated with one drop of concentrated hydrochloric acid and the mixture boiled for 2 min. It was added to water and the precipitate, in hot 2N-sodium hydroxide, was extracted with

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[5] Hey, Leonard, and Rees, *Chem. and Ind.*, 1962, 1025.

[6] Clarkson and Gomberg, *J. Amer. Chem. Soc.*, 1930, **52**. 2881.

chloroform. Removal of solvent from the dried extract gave 9,9′-spirobifluorene (0·02 g.). Acidification of the aqueous layer gave 9,9′-spirobifluorene-4-carboxylic acid (0·8 g.).

(*c*) By boron trifluoride. The acid (1 g.) in methanol (6 ml.) was treated with boron trifluoride–ether complex (6 ml.). Reaction commenced immediately and was completed by warming for 2 min., during which a white solid separated. The mixture was diluted with ether (30 ml.) and washed with water, and the ether layer dried and evaporated to give a residue (0·86 g.). Treatment of the residue with 2N-sodium hydroxide and ether separated it into 9,9′-spirobifluorene-4-carboxylic acid (0·6 g.) and methyl 9,9′-spirobifluorene-4-carboxylate, m. p. 170° (lit.,[1] m. p. 171—172°) (Found: C, 87·2; H, 5·0. Calc. for $C_{27}H_{18}O_2$: C, 86·6; H, 4·8%). Treatment of the acid (I) (1 g.) with boron trifluoride in ether gave 9,9′-spirobifluorene (0·01 g.) and 9,9′-spirobifluorene-4-carboxylic acid (0·9 g.).

Thermal decomposition of a mixture of the spiran-acid (III) *and the alcohol* (IV). The spiran-acid (III) and the alcohol (IV), when heated separately at 220°/2 mm., both sublimed unchanged. A mixture of the former (0·04 g.) and the latter (0·20 g.) was heated at 200° for 2 hr. and then sublimed at 220°/2 mm. The sublimate was extracted with aqueous-alcoholic potassium hydroxide, and the residue washed with water and dried, to give 9,9′-spirobifluorene (0·05 g.), m. p. 204—206° and mixed m. p. 206°.

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