Identification of Isomeric Di- and Poly-nitrobiphenyls by Mass Spectrometry

By **C. B. Thomas** * and **J. S. Willson**, Department of Chemistry, The University of York, Heslington, York YO1 5DD

On electron impact retention of positional identity occurs in the molecular ions of dinitrobiphenyls. This results in predictable differences between the spectra of the isomers and enables these compounds to be distinguished from one another. It is shown that the predictions as to the fragmentation sequences of dinitrobiphenyls can be extended to polynitrobiphenyls. Similarities have been found between the behaviour of a nitro-group and a carboxylic acid group in 2-substituted biphenyls and it is suggested that both functions are capable of effecting radical substitution into the adjacent aromatic ring.

THE oxidative coupling of a monosubstituted aromatic substrate can result in the formation of all six isomeric biphenyls, the separation of which may often be effected by gas chromatography. However, in the absence of authentic samples of the isomers, the correct assignment of the resultant peaks is difficult. We were recently faced with such a problem in connection with the oxidation of nitrobenzene [1] and decided to investigate the feasibility of using gas chromatography–mass spectrometry in solving it.

TABLE 1

Percentage of total ion current (Σ_{35}) borne by the ' structure-determining ' ions in the mass spectra of some nitrobiphenyls

Substituents	M	$M - OH$	$M - CO$	$M - NO$	$M - NO_2$	$M - NO$ $-CO$	$M - NO_2$ $-OH$	$M - NO_2$ $-CO$	$M - NO_2$ $-NO$	$M - NO_2$ $-NO_2$
4-Nitro	18·4			7·5	4·1	5·6				
3-Nitro	22·1			0·8	12·8	2·3				
2-Nitro	3·1	3·4	4·5	1·0	0·7	2·2				
4,4′-Dinitro	27·4			5·8	1·1	0·5	1·8		0·9	10·3
3,4′-Dinitro	18·8			5·0	2·5	2·3	1·3		0·9	13·2
3,3′-Dinitro	19·1			0·8	4·5	1·8	1·0		1·0	14·5
2,4′-Dinitro	16·3	3·0	0·5	0·8	1·1		1·0	7·5	3·6	4·3
2,3′-Dinitro	5·1	0·9	0·1	0·4	1·3	2·0	0·6	1·2	4·1	4·7
2,2′-Dinitro	0·1			0·1	28·3			1·6	7·9	0·7
2,4,4′-Trinitro	2·6	1·8	0·7	0·3	1·0	0·2	0·5	4·3	0·5	0·6
2,2′,4-Trinitro				0·2	18·6				0·8	0·8
2,2′,4,4′-Tetranitro	0·2			0·3	8·9				0·8	0·1

Frequently aromatic isomers have qualitatively similar mass spectra, possibly because partial or complete isomerisation of the molecular ions to a common intermediate occurs before fragmentation.[2] However, with certain substituents, of which the nitro-group can be one [3,4] positional identity is retained. Thus the spectra of *ortho*-substituted nitrobenzenes usually show unique features arising from an ' *ortho*-effect ' [5] while loss of nitric oxide occurs more readily from the molecular ion of the *para*-isomer than from that of the *meta*-compound.[3,6,7] The spectra of the three nitrobiphenyls are sufficiently different to confirm that positional identity is retained in this series.[8] Here the ' *ortho*-effect ' manifests itself in two ways, namely the loss of HO• and the successive loss of two molecules of carbon monoxide from the molecular ion, while the intensity of the M — NO peak in the spectrum of the *para*-compound is 10 times greater than that from the *meta*-isomer.

Dinitrobiphenyls.—We may reasonably expect positional identity to be retained in the molecular ions of the dinitrobiphenyls and their spectra, therefore, to show the same general trends as their mononitrated analogues. The intensities of the ' structure-determin-

---

[1] J. S. Willson, D. Phil. Thesis, York, 1971.

[2] F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *J. Amer. Chem. Soc.*, 1966, **88**, 5022; M. M. Bursey, *Org. Mass Spectrometry*, 1969, **2**, 907.

[3] R. H. Shapiro and J. W. Serum, *Org. Mass Spectrometry*, 1969, **2**, 533.

[4] B. Davis and D. H. Williams, *Chem. Comm.*, 1970, 412; R. Westwood, D. H. Williams, and A. N. H. Yeo, *Org. Mass Spectrometry*, 1970, **3**, 1485.

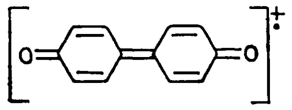
[5] G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc.* (*B*), 1971, 1273, and references therein; H. Budzikiewicz, C. Djerassi, and D. H. Williams, ' Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 399.

[6] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 5023.

[7] M. M. Bursey, *J. Amer. Chem. Soc.*, 1969, **91**, 1861; M. M. Bursey and M. K. Hoffman, *J. Amer. Chem. Soc.*, 1969, **91**, 5023.

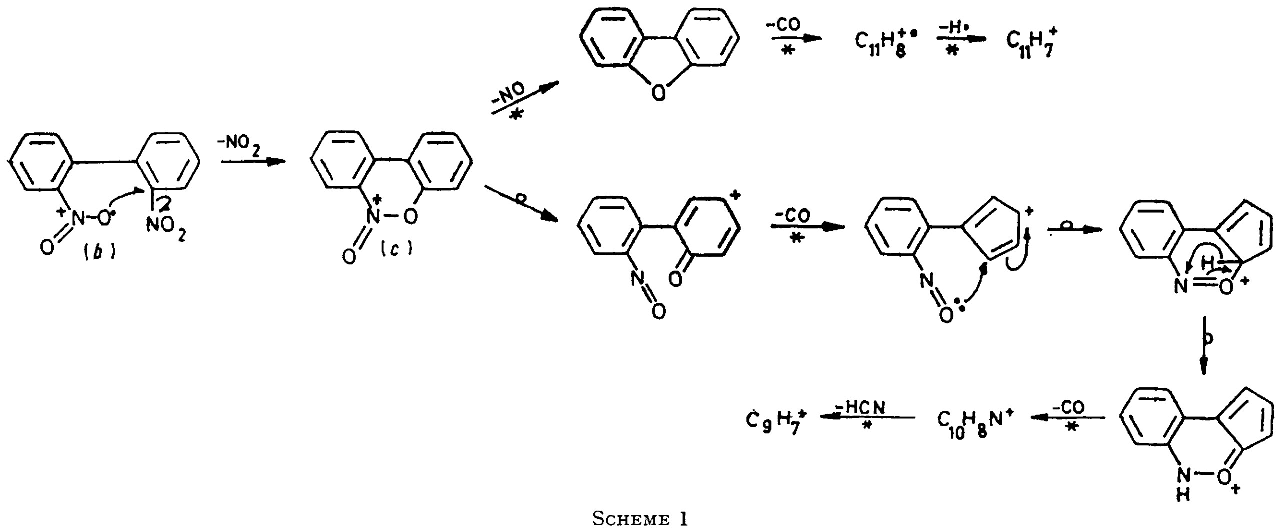
[8] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, **91**, 4974.

ing ' ions for the mono- and di-nitrobiphenyls and for three polynitrobiphenyls are set out in Table 1 from which it can be seen that this expectation is, in the main, borne out. Thus the 4,4′- and 3,3′-isomers display the *para*- and *meta*-modes of fragmentation respectively whilst 3,4′-dinitrobiphenyl, for which both modes can be operative, is intermediate in behaviour. Though positional identity is retained in the molecular ions the same is not true of the fragment ions. Thus, in all three cases, metastable peaks indicate that the $M - NO_2$ species fragment further by loss of an hydroxyl radical, a process assumed to be indicative of the presence of an *ortho*-nitro-group. If postulates laid down for odd-electron species are equally applicable to even-electron ions, the loss of the first nitro-group must have initiated extensive reorganisation of the carbon skeleton. On the other hand, in keeping with earlier observations,[4,9] the $M - NO$ ions appear to retain their original skeletons since only the 4,4′-isomer loses a second molecule of nitric oxide, presumably because, by so doing, it can attain the fully quinonoid structure (*a*).



(a)

The initial fragmentation of 2,2′-dinitrobiphenyl is substantially different from that of 2-nitrobiphenyl. Not only is the molecular ion of negligible intensity but no $M - OH$ species can be observed at all. Instead the base-peak of the spectrum corresponds to ejection of a nitro-group from the molecular ion. This may well be because displacement of one nitro-substituent by the other, as shown in Scheme 1, allows a more extensive overlap of the π-systems in the two aryl rings. The drawing of analogies between reactions occurring in solution and those taking place in the gas phase on electron impact is fraught with dangers but it is perhaps significant that the oxidation of 2′-nitrobiphenyl-2-carboxylic acid by lead tetra-acetate gives 3,4-benzocoumarin.[10] Lead tetra-acetate oxidations of carboxylic acids involve the generation of a carboxyl radical, at least when, as here, loss of carbon dioxide would lead to an unstable carbon radical,[10,11] and, in this case, cyclisation occurs by displacement of the nitro-group from the adjacent aromatic ring in a radical substitution process. If the molecular ion of 2,2′-dinitrobiphenyl is assumed to have the not unreasonable structure (*b*) with the radical site centred on the oxygen atoms, then the conversion of (*b*) into (*c*) is isoelectronic with the formation of 3,4-benzocoumarin. The decomposition of (*c*) involves loss of NO followed by further fragmentation reminiscent of that of dibenzofuran.[12]



Scheme 1

The spectra of 2,3′- and 2,4′-dinitrobiphenyl show the $M - OH$ and $M - CO$ fragments indicative of an *ortho*-nitro-substituent but it is not possible to clarify the position of the second substituent. Both compounds show a stronger $M - NO_2$ ion than an $M - NO$ ion indicating that reliance on the relative heights of these two peaks is not an absolute means of distinguishing between 3- and 4-substituted isomers. The 2,3′- but not the 2,4′-isomer shows a moderately intense ion arising by loss of nitric oxide and carbon monoxide from the molecular ion, a process which occurs more easily when a nitro-group is in a *meta*- rather than a

---

[9] F. Benoit and J. L. Holmes, *Chem. Comm.*, 1970, 1031.

[10] D. I. Davies and C. Waring, *J. Chem. Soc.* (*C*), 1967, 1639.

[11] W. H. Starnes, *J. Amer. Chem. Soc.*, 1964, **86**, 5603; J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 3609; J. K. Kochi, J. D. Bacha, and T. W. Bethea III, *J. Amer. Chem. Soc.*, 1967, **89**, 6538; D. I. Davies and C. Waring, *J. Chem. Soc.* (*C*), 1968, 2337.

[12] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.*, 1964, **17**, 975; J. H. D. Eland and C. J. Danby, *J. Chem. Soc.*, 1965, 5935; B. G. Pring and H. E. Stjernström, *Acta Chem. Scand.*, 1968, **22**, 549.

para-position. It is doubtful whether, without hindsight, such a distinction could have been relied on to differentiate the compounds unambiguously. Surprisingly this fragment is associated with a metastable peak showing it to originate directly from the molecular ion. Presumably a substantial proportion of the molecular ions lose the second neutral molecule very shortly after the first while still traversing the field-free region, thus lending support to the hypothesis[6] that the M — NO ions from *m*-nitrobenzenes are inherently unstable species.

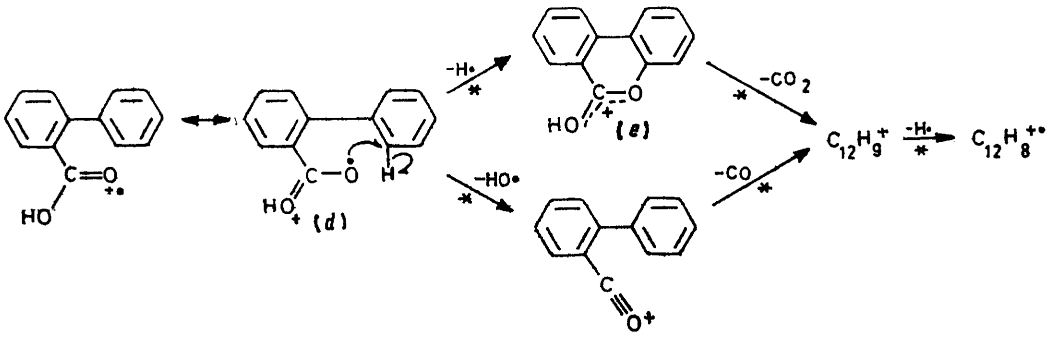
Polynitrobiphenyls.—To see whether the above generalisations could be extended to more complex compounds, we recorded the spectra of three polynitrobiphenyls. 2,4,4′-Trinitrobiphenyl shows the typical M — OH and M — CO ions of an *ortho*-substituted compound. The latter ion further fragments by successive loss of two nitro-groups to give strong peaks at *m/e* 215 and 169. [The facility with which nitro-groups are lost from the M — CO ion, a fragmentation mode noted also for 2,4′-dinitrobiphenyl, is evidenced by the fact that, even at 14 eV, these two ions and their appropriate metastable peaks are still present, in spite of the fact that the latter is a tertiary fragment.] Once again, however, the M — NO_2 ion is more intense than the M — NO ion making it impossible to predict the positions of the other two substituents.

The spectrum of 2,2′,4-trinitrobiphenyl resembles that of its 2,2′-dinitro relative. Thus the M — OH and M — CO ions are absent and the molecular ion and the M — NO species are of negligible intensity, displacement of a nitro-group giving rise to the base peak. The spectrum of 2,2′,4,4′-tetranitrobiphenyl shows the same general features with one interesting variation. A strong metastable peak indicates that the second most intense peak in the spectrum arises, at least in part, directly from the base peak (M — NO_2) by loss of 74 mass units. Accurate mass measurement of the parent and daughter ions show a difference in elemental composition of CNO_3 for which the most likely explanation is rapid sequential loss of NO_2 and CO. The *m/e* 214 ion also fragments in part by loss of 74 mass units (m^* observed at *m/e* 91·2) though metastable peaks for the successive loss of NO_2 and CO can also be discerned.

TABLE 2

Percentage of the total ion current (Σ_{35}) borne by the major ' structure-determining ' peaks in the mass spectra of diphenylcarboxylic acids

Substituents	M	$M - H$	$M - OH$	$M - OH$ $-CO$	$M - NO$	$M - NO_2$	$M - NO$ $-CO$	$M - OH$ $-NO_2$	$M - NO_2$ $-CO$
4-CO_2H	30·0		15·4	5·4					
2-CO_2H	17·0	8·6	16·3	6·3					
4-NO_2,2′-CO_2H	25·0	3·2	6·1	0·2	1·2	1·7	0·3	2·5	1·1
2-NO_2,2′-CO_2H			0·1	0·8		27·1		0·6	0·6



SCHEME 2

Nitrobiphenylcarboxylic Acids.—The possibility that the ready displacement of a nitro-group from the molecular ion of 2,2′-dinitrobiphenyl is essentially a radical process, and its apparent similarity to the lead tetra-acetate induced cyclisation reaction[10] prompted us to look at the spectrum of 2′-nitrobiphenyl-2-carboxylic acid. To determine how a 2-carboxy-function in a biphenyl could modify the mode of fragmentation we recorded the spectrum of biphenyl-2-carboxylic acid and, for comparison, that of its 4-isomer for which any ' *ortho*-effect ' should be inoperative. Table 2 lists the principal ions, from a structure determining point of view, of these two acids together with those of 2′- and 4′-nitrobiphenyl-2-carboxylic acids.

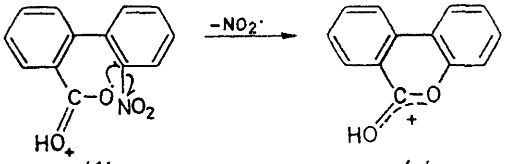
Both the monofunctional compounds show, as the principal decomposition mode, the successive loss of HO•, CO, and H•. The two spectra differ qualitatively in only one major aspect: that of the *ortho*-isomer shows a strong M — 1 ion which is completely absent from that of the *para*-compound. This we can attribute to interaction between the *ortho*-substituents and a logical mode of elimination of a hydrogen atom is shown in Scheme 2 [(*d*) ⟶ (*e*)]. This is an almost identical radical displacement to that outlined in Scheme 1 for substitution into the neighbouring aromatic ring by a nitro-group. Deuterium labelling of the 2′-positions is unlikely to confirm this scheme since randomisation of the aromatic hydrogen atoms in the molecular ion will probably occur before fragmentation.[13]

The $M - H$ ion subsequently loses carbon dioxide (m^* observed) and may also lose a hydroxy-group and a carbon monoxide molecule since $M - 18$ and $M - 29$ peaks are absent from the spectrum of the *para*-isomer. It is not possible to say whether the processes typical of an *ortho*-nitro-group, namely loss of HO· or CO from the molecular ion by *ortho*-interaction, also occur for a carboxylic acid group. For the former there exists an alternative means of production of the hydroxyl radical and, in the case of the latter, although a weak $M - 28$ ion can be observed, this is also present in the spectrum of the 4-carboxylic acid.

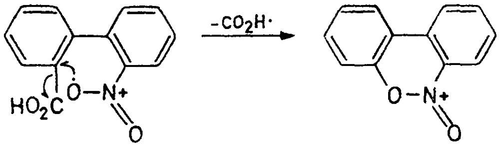
4′-Nitrobiphenyl-2-carboxylic acid behaves on electron impact much as expected, with the loss of H· and of HO· being attributable to fragmentation initiated by the acid function, whilst the ejection of NO followed by CO and of NO_2 is associated with the nitro-function. The spectrum of 2′-nitrobiphenyl-2-carboxylic acid strongly supports the view that the carboxylic acid group resembles the nitro-group in being able to effect radical substitutions. Thus the molecular ion is completely absent and only a miniscule $M - OH$ fragment can be observed. The base peak of the spectrum is at *m/e* 197 which can be readily explained in terms of a radical displacement of the nitro-group by the neighbouring carboxylic acid substituent [(*f*) ⟶ (*g*)]. An alternative fragmentation involving displacement of the acid function by the nitro-group [(*h*) ⟶ (*i*)] may also occur to a minor extent since the intensity of the ion *m/e* 198 (4·7% of the total ion current), is significantly greater than would arise solely from the ^{13}C isotope peak of *m/e* 197 (3·9%). An attempt at the accurate mass measurement of this minor ion failed to confirm its elemental composition because of interference from the major constituent of *m/e* 198. However, loss of $\cdot CO_2H$ could also occur by the typical carboxylic acid fragmentation route (successive loss of HO· and CO) without the aid of the nitro-substituent.

Three possibilities suggest themselves as explanations for the preferred displacement of the nitro-group by the acid group rather than *vice versa*. First, a nitro-group might be a more easily displaced substituent than the carboxy-group. Certainly e.s.r. studies suggest that $\cdot NO_2$ is the more stable species in solution. It can be observed in a number of static solvents[14] whereas $\cdot CO_2H$ has only been observed as a transient intermediate in a flow system.[15] In addition a carbon–nitrogen bond is weaker than a corresponding carbon–carbon bond[16] and therefore more easily broken. Secondly, the oxy-radical (*f*) may be a better attacking species than (*h*) as the adjacent carbon atom in (*f*) is less electronegative than the nitrogen atom in (*h*). Thirdly, the electron deficiency in the molecular ion might be located preferentially on the carboxylic acid group. In view of the observation that the ionisation potential of benzoic acid[17] is significantly lower than that of nitrobenzene[18] this is a not unreasonable supposition.

The other principal ions in the spectrum of this compound are derived from *m/e* 197. Thus successive loss of two molecules of carbon monoxide and one of acetylene account for *m/e* 169, 141, and 115 whilst ejection of carbon dioxide followed by one or two protons accounts for *m/e* 153, 152, and 151. A metastable peak is observed both for this compound and for its 4′-isomer showing that the ion *m/e* 197 decomposes, in part, by loss of water though this fragmentation is not easy to rationalise. The only other peak of significance is *m/e* 168 which presumably corresponds to the dibenzofuran molecular ion and is the origin of *m/e* 140 and 139.[12] A possible source of it is the ($M - CO_2H$) ion (*i*) (*cf.* 2,2′-dinitrobiphenyl).



(*f*) (*g*)



(*h*) (*i*)

EXPERIMENTAL

Mass spectra were recorded on an AEI MS 12 spectrometer operating, unless stated otherwise, at 70 eV. Samples were introduced into the source, maintained at 100—120°, by means of a direct insertion probe except in the case of 2,3′-dinitrobiphenyl. This compound, which could not be isolated in a pure state, was separated from impurities on a gas chromatograph (Pye 104, model 24; 5 ft × ¼ in column packed with 10% silicone SE 30 coated on Celite) and the peak fed directly into the spectrometer *via* a stainless-steel capillary and a Watson–Biemann separator. Care was taken to ensure that the concentration of sample remained essentially constant during the scans and that the spectrometer had fully stabilised. Accurate mass measurements were carried out on an AEI MS 902 spectrometer by the Physico-Chemical Measurements Unit,

---

[13] J. G. Burr, J. M. Scarborough, and R. H. Shudde, *J. Phys. Chem.*, 1960, **64**, 1359.

[14] B. H. J. Bielski and J. M. Gebicki, *J. Phys. Chem.*, 1969, **73**, 1403.

[15] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389; A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 400; D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1970, 1083.

[16] E. G. Lovering and K. J. Laidler, *Canad. J. Chem.*, 1960, **38**, 2367; G. I. Levi and A. A. Balandin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 157.

[17] A. Foffani, S. Pignatoro, B. Cantone, and F. Grasso, *Z. phys. Chem.* (*Frankfurt*), 1964, **42**, 221.

[18] G. F. Crabbe and G. L. Kearns, *J. Phys. Chem.*, 1962, **66**, 436.

Aldermaston. Full details of all spectra discussed in this paper are being submitted to the Mass Spectrometry Data Centre for inclusion in their files. M.p.s were on a Kofler micro-hot stage.

Materials.—2- and 4-Nitrobiphenyl and biphenyl-4-carboxylic acid were commercial samples (Koch–Light) and were recrystallised before use. 3-Nitrobiphenyl was available within this laboratory. 2,2′-, 2,4′-, and 4,4′-dinitrobiphenyl, 2,2′,4- and 2,4,4′-trinitrobiphenyl, and 2,2′,4,4′-tetranitrobiphenyl were prepared by the methods of Gull and Turner.[19] Recrystallisation from ethanol gave 2,2′-dinitrobiphenyl (yellow crystals), m.p. 124—124·5° (lit.,[19] 123—124°), 2,4′-dinitrobiphenyl (yellow prisms), m.p. 94—95° (lit.,[19] 92·5—93·5°), and 4,4′-dinitrobiphenyl (pale yellow needles), m.p. 241—244° (lit.,[19] 239—243°). Recrystallisation from glacial acetic acid gave 2,2′,4-trinitrobiphenyl (pale yellow rhombs), m.p. 149—150° (lit.,[19] 150—151°), 2,4,4′-trinitrobiphenyl (yellow needles), m.p. 176—178° (lit.,[19] 175—176°), and 2,2′,4,4′-tetranitrobiphenyl (yellow amorphous powder), m.p. 164—166° (lit.,[19] 165°). It was observed that compounds containing 2,2′-dinitro-substituents darkened markedly over a period of time.

2,3′-, 3,3′-, and 3,4′-Dinitrobiphenyls were prepared by Ullmann reactions using the appropriate iodonitrobenzenes and copper bronze in the manner described by Davey and Latter.[20] 3,3′-Dinitrobiphenyl had m.p. 204—206° (yellow needles from methanol) (lit.,[21] 200°). 3,4′-Dinitrobiphenyl, m.p. 183—186° (lit.,[22] 187—189°) was obtained as buff crystals by repeated recrystallisation from methanol. 2,3′-Dinitrobiphenyl could not be separated from isomeric materials and was introduced into the mass spectrometer *via* a gas chromatograph.

Biphenyl-2-carboxylic acid, m.p. 110—111° (lit.,[23] 112—113°) was obtained by the reaction of fluorenone with potassium hydroxide after the manner of Hey *et al.*[23] Nitration [23] of this acid gave 2′-nitrobiphenyl-2-carboxylic acid, m.p. 166—170° (white crystals from chloroform) (lit.,[23] 168, 170°), and 4′-nitrobiphenyl-2-carboxylic acid, m.p. 231—234° (white needles from ethanol) (lit.,[23] 231°).

One of us (J. S. W.) thanks the S.R.C. for a studentship.

[1/1604 *Received, 3rd September*, 1971]

---

[19] H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 1929, 491.

[20] W. Davey and R. W. Latter, *J. Chem. Soc.*, 1948, 264.

[21] J. Forrest, *J. Chem. Soc.*, 1960, 594.

[22] Y. Mizuno and D. Simamura, *J. Chem. Soc.*, 1958, 3875.

[23] D. H. Hey, J. A. Leonard, and C. W. Rees, *J. Chem. Soc.*, 1962, 4579.