The Synthesis of Dibenzo[*fg*,*op*]naphthacene† from Biphenylene and Lithium

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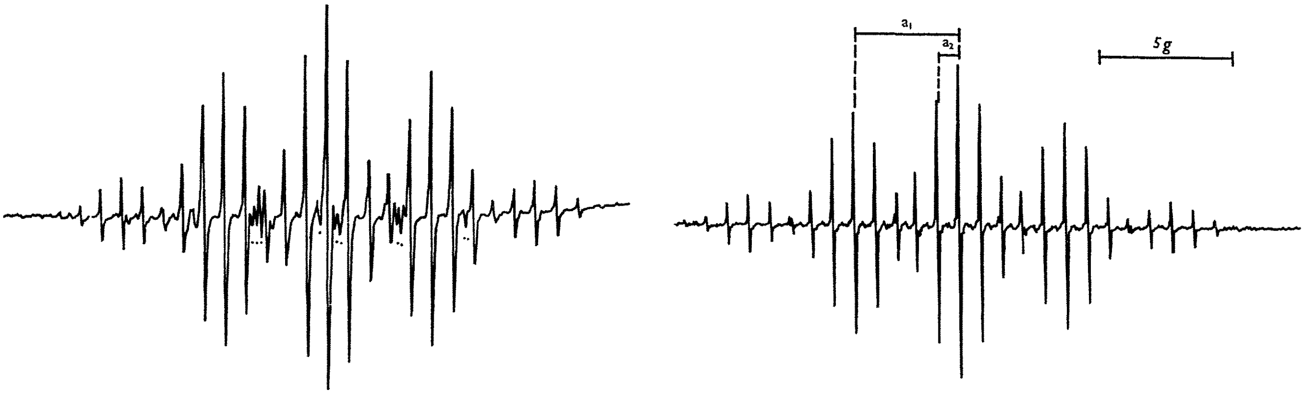
DURING an e.s.r. study of the biphenylene radical anion with a variety of solvents and counterions[1] an unusual coupling reaction was observed. In 2-methyltetrahydrofuran (MTHF) in the presence of lithium metal, biphenylene eventually produces a solution which exhibits the e.s.r. spectrum of the dibenzo[*fg*,*op*]naphthacene radical anion.

Biphenylene (2—3 mg.) and clean lithium (0·1 g.) were placed in a 10 mm. o.d. tube with a side-arm designed to fit into the microwave cavity of an e.s.r. spectrometer. MTHF (1 ml.) was vacuum-distilled into the evacuated tube, which was then sealed. After several days at room temperature the solution turned red and exhibited a 35-line e.s.r. spectrum shown in the Figure (a). The spectrum of the radical anion of dibenzo[*fg*,*op*]naphthacene ("DBN") prepared by reaction with lithium is shown in the Figure (b). Analysis of each spectrum in terms of the basic hyperfine splittings is given in the Table.

By analogy with the pyrene radical anion hyperfine splittings[3] the large (4·09 *g*) hyperfine splitting probably arises from the 1, 3, 8, and 10 protons. The small (0·84 *g*) hyperfine splitting must arise from accidental degeneracy of the protons at the 2- and 9-positions with protons either at



(a) (b)

FIGURE. (a) *Spectrum of* Li^+DBN^- *showing some unreacted* Li^+ biphenylene$^-$ (*indicated by dot*) *in MTHF at* −50°. (b) *Spectrum of* Li^+ DBN^- *at* −50° *in MTHF.*

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† Less preferred alternative name: dibenzo[*e*,*l*]pyrene.

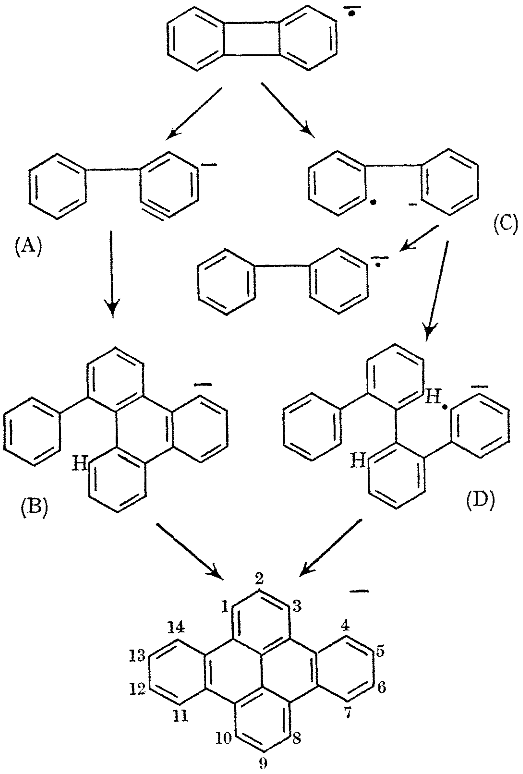
TABLE

Hyperfine splittings of the dibenzo[fg,op]*naphthacene* ["DBN"] *anion radical*

Hyperfine splitting[a]	Product of biphenylene and Li (−62°) [Fig. (b)]	Li $^{+}$DBN^{-} in MTHF (−71°)	K^{+}DBN^{-} in 1,2-dimethoxyethane
$a^{\rm H}(4)$	4·087 ± 0·010	4·090 ± 0·010	4·124 ± 0·010
$a^{\rm H}(6)$	0·832 ± 0·010	0·834 ± 0·010	0·846 ± 0·010

[a] $a^{\rm H}(n)$ refers to a proton hyperfine splitting for n equivalent protons.
[b] See ref. 2, errors estimated.

the 4-, 7-, 11-, and 14-positions or at the 5-, 6-, 12-, and 13-positions. One of the latter two sets of protons must have a hyperfine splitting less than 0·015 *g* since no splitting is detected. This analysis is confirmed by HMO and McLachlan[4] calculations.



The very strong e.s.r. signal obtained indicates that the yield is high. There are no other paramagnetic products present, in particular, no spectrum assignable to the *o*-quaterphenyl anion radical could be seen. It is interesting that the reaction of biphenylene in ether solvents with other alkali metals yields only the biphenylene radical anion[5] and the dianion. Such samples are stable for several months although solutions of sodium and potassium biphenylenide tend to decompose to form the biphenyl radical anion if the solution becomes too concentrated or if it is left for several months. A spectrum corresponding to lithium biphenyleneide can be obtained if the reduction with lithium proceeds for only a few hours. To obtain this spectrum under these conditions larger quantities of lithium and biphenylene were used. If the reaction is allowed to continue at room temperature for several hours more the spectrum of DBN^{-} appears. The Figure (a) shows the spectrum of DBN^{-} with some unreacted biphenylene anion at −50°. A spectrum of the biphenyl radical was observed in a concentrated reaction solution at temperatures between −40 and −80°; the spectrum disappeared after the solution was kept at room temperature for about 1 hr. This may be caused by protonation of the intermediate by the solvent, or by traces of lithium hydroxide.

Two mechanisms may be suggested to account for this reaction. The first involves a benzyne-type intermediate (A), which adds to neutral biphenylene to form intermediate (B). This mechanism seems unlikely, since Heaney and Lees[6] reported that benzyne does not add to biphenylene under the conditions of our reaction. The second mechanism involves a biphenyl-like intermediate (C) which adds to biphenylene to form intermediate (D), which upon dehydrogenation forms the DBN radical anion. This latter mechanism is supported by the fact that DBN has been obtained by cyclic dehydrogenation of *o*-quaterphenyl using lithium in ether.[7] Yields of DBN however, were about 2%. Further support comes from the fact that in more acidic ether solvents, such as 1,2-dimethoxyethane, protonation of intermediate (C) leads to the biphenylide ion which is the only product observed. In diethyl ether, however, only the biphenylene radical anion and dianion are observed. This is presumably a result of the poorer solvation by diethyl ether.

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