

boron trifluoride etherate. The specifically labeled phylloquinones were synthesized from phytol and the corresponding 2-methyl-1,4-naphthoquinones (menadiolone) which had been selectively labeled with  $^{18}\text{O}$  by taking advantage of the 50-fold difference in the acid-catalyzed rate of exchange between the O-1 and the O-4 positions; conversion to phylloquinones proceeded without loss of label. The  $^{18}\text{O}$  content ( $\pm 0.15\%$ ) was established by mass spectrometric analysis of the CO resulting from pyrolysis of the quinones at  $500^\circ$ .

The biological system and quinone isolation were as previously described<sup>3d</sup> except that additional chromatography on 5% silver nitrate impregnated Kiesel gel removed any native quinone [MK-9( $\text{H}_2$ )] not destroyed by partial light inactivation. All experiments (Table I) displayed phosphate fixation coupled to oxidation. Recovered quinone showed complete retention of isotope (Table II) except for a slow loss roughly proportional to the exposure time of quinone to the medium, which probably occurred *via* simple exchange of the carbonyl functions with water. That such exchange is not related to oxidative phosphorylation is established by the parallel exchange in the KCN-treated system (expt 4) where no consumption of oxygen occurred.

Notable is the absence of exchange in the anaerobic-aerobic expt 3. The effect of this cycle should be to form and then oxidize any reduced species,<sup>5</sup> thus increasing the fraction of phylloquinone involved in oxidative phosphorylation relative to a possible small fraction in the steady-state aerobic case. Since no enhancement of exchange occurred, such a phosphorylated intermediate, if formed, was not formed by any of the schemes shown.

Our evidence for the absence of quinone oxygen exchange says that quinone involvement in oxidative phosphorylation must proceed with the original carbon-oxygen bonds remaining intact. Since this is a negative result, conceivably such exchange did occur but to an undetectably small extent, *i.e.*, less than 0.3%, the accuracy of our analysis. This limitation, plus the anaerobic-aerobic experiment, make it extremely unlikely that oxygen exchange is involved in the quinone's role in oxidative phosphorylation.

(5) P. J. Russel and A. F. Brodie, *Biochim. Biophys. Acta*, **50**, 76 (1961); D. Gutnick, T. Watanabe, and A. F. Brodie, *Federation Proc.*, **25**, 530 (1966); T. Watanabe and A. F. Brodie, *Proc. Natl. Acad. Sci. U. S. A.*, **56**, 940 (1966).

(6) National Institutes of Health Predoctoral Fellow.

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Received October 20, 1966

## Pyrolysis of Biphenylene<sup>1</sup>

Sir:

Biphenylene, upon electron impact,<sup>2</sup> gives a relatively abundant ion at  $m/e$  76 (13.4% relative intensity). By comparing the ratios of intensities of the  $m/e$  peaks at 76 (13.4) to 152 (100) and 76.5 (1.3) to 153 (12.9), it is estimated that the contribution of doubly charged ion at  $m/e$  76 is about 75%. The balance, *i.e.*, 25%, is an ion of mass 76 and presumed to be benzyne.<sup>3</sup>

(1) Supported in part by the Case Research Fund.

(2) L. Friedman, N. Ingber, and D. F. Lindow, unpublished data.

In attempts to generate benzyne thermally<sup>4</sup> 1:1 mixtures of biphenylene<sup>6</sup> and anthracene were pyrolyzed at  $\sim 440^\circ$  in a sealed Vycor tube (liquid phase) or in the gas phase.<sup>7</sup> It was assumed that formation of triptycene<sup>8</sup> would be indicative of the presence of benzyne. In these experiments little, if any, biphenylene was recovered, and triptycene was not detected.

The sealed tube experiments in the presence or absence of anthracene gave only one major product. This was found to be tetraphenylene<sup>9,10</sup> (tetrabenzocyclooctatetraene) on the basis of melting point ( $232\text{--}233^\circ$ , cor) and infrared, ultraviolet, and mass spectra. A minor by-product is biphenyl.<sup>11</sup>

Tetraphenylene was obtained in 96% yield by pyrolysis ( $400^\circ$ ) of biphenylene in an evacuated sealed tube.<sup>12,13</sup> The effects of time and temperature on the course of the reaction are listed in Table I. Lower

Table I. Pyrolysis of Biphenylene (Sealed Tube)

Run	T, °C	Time, hr	Tetra-phenyl-ene, %	Bi-phenyl, %	Bi-phenyl-ene, %
1	395-408	1	96	4	0
2	430-445	0.5	85	3	0
3	430-445	18	66	5	0
4	330-350	1	5	0	95
5	330-350	6	11	1	76
6	330-350	30	11	6	17

yields at higher temperatures and extended reaction times indicate thermal destruction of tetraphenylene (*cf.* runs 1-3). Lower temperatures result in decreased conversion of biphenylene; however, by extending the

(3) (a) R. S. Berry, J. Clardy, and M. E. Schafer, *J. Am. Chem. Soc.* **86**, 2738 (1964). For other examples of electron-impact fragmentation leading to  $m/e$  76 ions (presumably benzyne) see: (b) F. W. McLafferty and R. J. Gohlke, *Anal. Chem.*, **31**, 2076 (1959); (c) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965), *J. Org. Chem.*, **31**, 3307 (1966); (d) R. F. C. Brown and R. K. Solly, *Australian J. Chem.*, **19**, 1045 (1966).

(4) Electron-impact and thermal fragmentation may or may not lead to similar results. For example, the results from electron-impact and thermal fragmentation of phthalic anhydrides<sup>3c,5</sup> and indantrione<sup>3d</sup> parallel each other while those from anthraquinone and fluorenone do not.<sup>3d</sup>

(5) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).

(6) Obtained in  $\sim 30\%$  yield from benzenediazonium-2-carboxylate: L. Friedman and A. Seitz, *in press*.

(7) Reaction effected in an oven (helium atmosphere) connected directly to a dual column (7 ft  $\times$  14 in. o.d. 3% GE SF 1093 on acid-washed DMCS-treated Chromosorb G, 70-80 mesh) F & M gas chromatograph. The authors acknowledge with thanks Dr. Stephen S. Hirsch and Mr. Gazie K. Ragep, Chemstrand Research Corp., for performing these experiments.

(8) Under these conditions triptycene remains essentially unchanged.

(9) G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957). In an excellent paper on biphenylene chemistry, it was stated that "diphenylene is extraordinarily stable—it is formed at  $350^\circ$ ." However, in the discussion J. Chatt reported that biphenylene and bis(triphenylphosphino)nickel dicarbonyl at  $100^\circ$  for 7 hr gave tetraphenylene ( $\sim 10\%$ ) as the only isolable product: W. Baker and J. F. W. McOmie, "Diphenylene and the Cyclobutadiene Problem," in the Chemical Society Symposia, Bristol, 1958, Special Publication No. 12, The Chemical Society, London, 1958, pp 49-67.

(10) Vapor-phase pyrolysis gave, in addition to tetraphenylene and biphenyl, triphenylene and significant amounts of a large number of as yet unidentified hydrocarbons.

(11) (a) Another possible by-product is *o*-quaterphenyl which was not separable from tetraphenylene *via* glpc. On the basis of infrared analysis (ultraviolet analysis does not distinguish between them) not more than 1% could be present in the crude tetraphenylene. (b) Mass spectral data indicates that hexaphenylene may be present ( $< 1\%$ ).

(12) Large-scale (20 g) pyrolysis of biphenylene was conducted in a small (40 ml) stainless-steel bomb at  $375^\circ$  for 1 hr.

(13) Small amounts ( $\sim 1\%$ ) of tetraphenylene were also obtained by photolysis of biphenylene (0.066 M) in hexane at 2538 and 3500 Å. Solid films were unaffected.

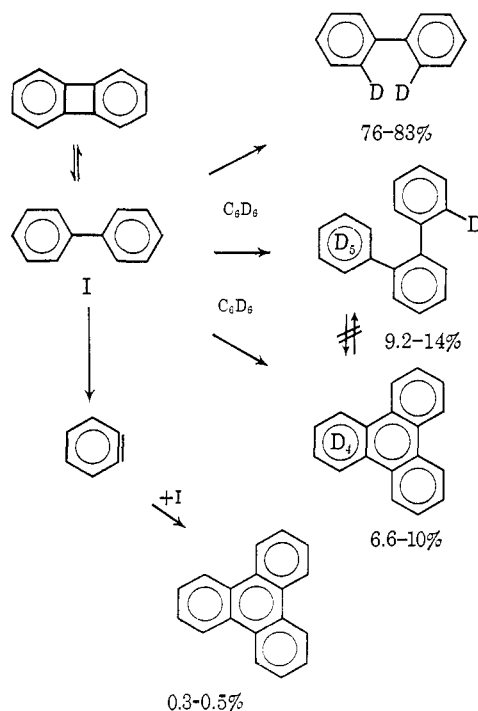


Figure 1. Pyrolysis of biphenylene: products and composition (28–35% yield based on unrecovered biphenylene).

reaction time, biphenylene is gradually consumed without significant formation of tetraphenylene. The non-volatile portion of the reaction mixture is polymeric.<sup>14</sup>

Thus it seems most likely that efficient dimerization occurs in the liquid phase at higher temperatures as a result of the relatively high steady-state concentration of the diradical, I. At lower temperatures, the concentration of I would be smaller; consequently dimerization would be less favored, and radical addition presumably occurs (Table I, runs 4–6) to give polymeric material.

Other evidence for the intermediacy of I was obtained by vapor-phase pyrolysis of biphenylene (0.1 M) in benzene and benzene- $d_6$ , respectively, between 650 and 730° with contact times of 3–5 sec. In benzene at 650°, for example, in addition to unreacted biphenylene (~70%), three major products were obtained: biphenyl, triphenylene (1.3%), and *o*-terphenyl (2.1%).<sup>15a</sup> Only trace amounts of tetraphenylene were detected. At 730°, the results were qualitatively the same but more biphenylene was consumed. However, in the absence of biphenylene, smaller amounts of biphenyl and *o*-terphenyl are formed.<sup>16</sup> When the pyrolysis was conducted in benzene- $d_6$  (Figure 1) at 650° the biphenyl consisted of mainly  $d_2$  (28%) and  $d_{10}$  (57%) species.<sup>16</sup> Biphenyl- $d_2$  is formed from I and benzene- $d_6$  by deuterium abstraction, while biphenyl- $d_{10}$  arises mainly from pyrolysis of benzene- $d_6$ .<sup>16,17</sup> The presence of other deuterated species is a result of deuterium-hy-

drogen exchange<sup>18</sup> between benzene- $d_6$  and biphenylene<sup>19</sup> and/or biphenyl- $d_2$ . The triphenylene and *o*-terphenyl<sup>20</sup> contained mainly four and six deuterium atoms/molecule, respectively, and more highly deuterated species<sup>19</sup> formed by exchange reactions in the expected amounts. At 730°, the anticipated increase in hydrogen–deuterium exchange was observed.

The presence of triphenylene- $d_0$  (5.2%) is best explained by the reaction of I with benzyne- $d_0$  from fragmentation of biphenylene or preferably I. To support this contention, biphenylene was pyrolyzed at 735° in a nitrogen stream. In addition to recovered biphenylene (relative peak area, 100) and tars, the volatile products were biphenyl (44), tetraphenylene (1.2), triphenylene (7.4), and at least six other higher boiling unidentified hydrocarbons (~50). Thus it appears that I is an efficient trap for the benzyne produced since naphthalene- $d_4$  was not, but triphenylene- $d_0$  was, observed in pyrolyses conducted in excess benzene- $d_6$ .<sup>3c,d</sup> These results are consistent with those outlined in Figure 1. This may account for the formation of triphenylene by the supposed trimerization of benzyne.<sup>3c,d</sup>

The lack of appreciable further fragmentation (<0.5%) of I in the presence of benzene is not surprising since I undergoes other reactions with benzene (Figure 1). However, in the absence of benzene, in the gas phase where dimerization and other bimolecular reactions are minimized I undergoes more extensive fragmentation to benzyne. This is in closer agreement with electron-impact data.<sup>4</sup>

**Acknowledgment.** The authors are indebted to Mr. Linwood B. Crider, B. F. Goodrich Company, for mass spectral analyses.

(18) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 21 (1966).

(19) Biphenylene (84%  $d_0$ , 14%  $d_1$ , 1.5%  $d_2$ , and 0.2%  $d_3$ ) recovered from pyrolysis in benzene- $d_6$  at 650° exhibited, as expected, less deuterium-hydrogen exchange than that at 730° (49%  $d_0$ , 32%  $d_1$ , 14%  $d_2$ , 3.9%  $d_3$ , 0.9%  $d_4$ , and 0.4%  $d_5$ ). The levels of exchange observed parallel that in all of the reaction products.

(20) Under these conditions triphenylene and *o*-terphenyl are essentially (<1%) noninterconvertible, and tetraphenylene does not fragment.

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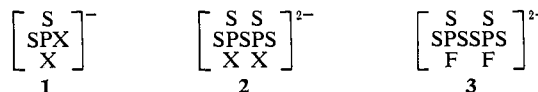
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Received November 21, 1966

## New Phosphorus–Sulfur Chemistry

Sir:

A new class of anionic substituted thiophosphates has been prepared by the reactions of certain types of metal salts with tetraphosphorus decasulfide. These preparations were effected in heterogeneous systems using media such as water, acetonitrile, or 1,2-dimethoxyethane. Three structural species were obtained as exemplified by 1–3.<sup>1</sup> The type of product, isolated



(1) Sample analytical data for these salts are as follows: *Anal.* Calcd for  $(n-C_3H_7)_4N^+S_2P(N_3)_2^-$  (mp 75–76.5°): C 39.4; H, 7.7; N, 26.8; P, 8.5; S, 17.5. Found: C, 39.5; H, 7.8; N, 26.6; P, 8.6; S, 17.7. Calcd for  $(n-C_3H_7)_4N^+S_2PCN(CSNH_2)^-$  (mp 114–115° dec): C, 45.7; H, 8.2; N, 11.4; P, 8.4; S, 26.2. Found: C, 45.9; H, 8.2; N, 11.3; P, 9.0; S, 26.5. Calcd for  $[(n-C_3H_7)_4N^+]_2[S_2P(N_3)SP(N_3)S_2]^{2-}$  (mp 157°): C, 42.5; H, 8.3; N, 16.5; P, 9.1; S, 23.6. Found: C, 42.4; H, 8.7; N, 16.3; P, 9.2; S, 23.7.

(14) The nature of this substance is presently under investigation.

(15) (a) Typical data. (b) Other hydrocarbons are also formed. Two of them were tentatively identified as 1- and 2-phenylbiphenylenes via mass spectrometry. On the basis of glpc and mass spectral data *o*-, *m*-, and *p*-terphenyl were also present.<sup>16</sup>

(16) G. M. Badger, *Progr. Phys. Org. Chem.*, **3**, 1 (1966).

(17) (a) The portion of biphenyl from I and benzene- $d_6$  amounts to 38.2% (3.7%  $d_1$ , 28.3%  $d_2$ , 5.5%  $d_3$ , and 0.7%  $d_4$ ) and that from dimerization of benzene- $d_6$  and possibly phenyl- $d_5$  radicals (from I and benzene- $d_6$ ) amounts to 59.3% (2.1%  $d_3$ , 57.2%  $d_{10}$ ).