Reactions of Fluorenones and Tetraphenylcyclopentadienones with Tricovalent Phosphines and Phosphites[1]

IRVING J. BOROWITZ,*[2] MORRIS ANSCHEL, AND PHILIP D. READIO

Department of Chemistry, Belfer Graduate School of Science, Yeshiva University, New York, New York 10033, and Lehigh University, Bethlehem, Pennsylvania 18015

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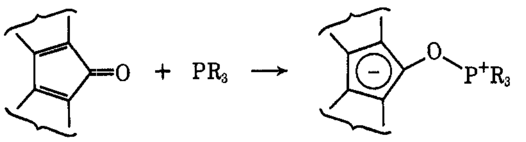
Fluorenone (**3**) or 2,7-dibromofluorenone (**4**) react with triethyl phosphite (TEP) to give carbanion oxyphosphonium dipoles which react with a second mole of ketone to give 2:1 adducts of pentaoxyphosphoranes. Reaction of **3** or **4** with tributylphosphine (TBP, neat) gives the corresponding bifluorenylidine, while reaction in solvents which contain abstractable hydrogen gives the corresponding fluorene, bifluorenyl, and tribiphenylenepropane. These reactions are rationalized as proceeding through carbene or carbenoid species. The phosphoranes are thermally rearranged to biphenylenephenanthrones and are converted to oxazolines upon reaction with acetonitrile. Initial reaction of **3** or **4** with TEP at higher temperatures gives the phenanthrones directly. Tetraphenylcyclopentadienone (**1**) reacts with TBP to give dihydrooctaphenylfulvalene and a $C_{58}H_{40}$ hydrocarbon which is also obtained from **1** upon reaction with triphenylphosphine. Other ketones, which cannot form stabilized carbanion adducts, do not react with TEP or TBP under similar or more strenuous conditions.

Ketones such as tetraphenylcyclopentadienone (**1**), 2,3-diphenylindenone (**2**), or fluorenone (**3**) should have enhanced reactivity toward P(III) reagents, when compared with simple ketones which are mainly unreactive.[3] The reactivity is expected to be due to the formation of 1,3-carbanion oxyphosphonium dipoles such as i wherein the negative charge is delocalized in a cyclic-6-π-electron system.



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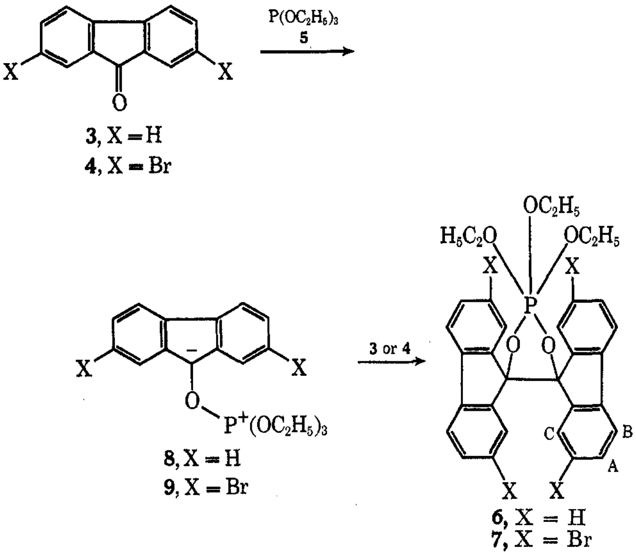
Fluorenone (**3**) or 2,7-dibromofluorenone (**4**) reacts with triethyl phosphite (**5**, TEP) at room temperature to give 2,2,2-triethoxy-4,5-bisbiphenylene-1,3,2-dioxaphospholane (**6**), or the corresponding tetrabromo derivative **7**.[3-5] These reactions are interpreted as occurring *via* the further reaction of the 1,3 dipoles **8** and **9** with a second mole of ketone (Scheme I).

Attempts to trap the postulated species **8** with acenaphthalene or benzaldehyde failed in that only the usual product **6** was obtained. A competition of **3** and **4** for **5** gave only **7** (71%).

The phosphoranes are fairly stable solids characterized by their ^1H and ^{31}P nmr spectra. Thus **6** has ^{31}P nmr absorption at +48 ppm ($CDCl_3$, *vs.* 85% H_3PO_4)[6] which is related to similar values for other pentaoxyphosphoranes.[4,7]

SCHEME I



The key intermediates in these reactions are the postulated dipolar species **7** and **8**. The isolation of such a species, from the reaction of **1** with tris(dimethylamino)phosphine,[8] and the reactions of **3**, hexafluoracetone, and trifluoroacetophenone with tris(dimethylamino)phosphine[4b] lend support to our arguments on the intermediacy of these species. The initial site of attack in the formation of **6** or **7**, and the related phosphoranes isolated by Ramirez[4] remains a problem.

It may be best to defer the question of the detailed mechanistic pathways involved and to concentrate on the factors which stabilize one or another of the forms of the 1:1 adducts. In the present work it is clear that stabilized carbanions allow further reaction of P–O–C forms.[9]

Reactions of the Phosphoranes.—When **6** or **7** is heated under a variety of conditions, two reactions occur: (a) reversion to the fluorenone, and (b) rearrangement to the 9-biphenylenephenanthrones **10** and **11**. The relative extent of the two reaction path-

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(2) To whom correspondence should be addressed at the Belfer Graduate School of Science, Yeshiva University, New York, N. Y. 10033.

(3) (a) I. J. Borowitz and M. Anschel, *Tetrahedron Lett.*, 1517 (1967); (b) See correction, *ibid.*, 5032 (1967).

(4) (a) The formation of **6** and related phosphoranes from other trialkyl phosphites has also been noted by F. Ramirez and C. P. Smith, *Chem. Commun.*, 662 (1967); (b) for related reaction of fluorenones, hexafluoroacetone, and trifluoroacetophenone, see F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6283 (1967).

(5) For a review of oxyphosphoranes see F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

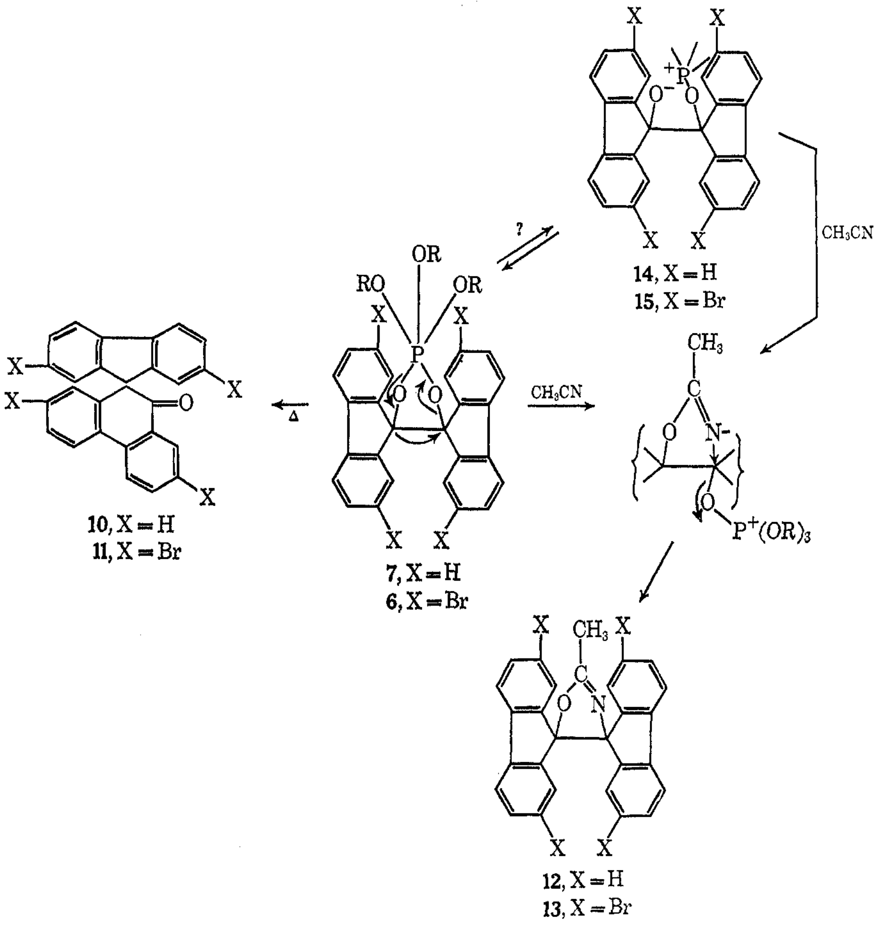
(6) ^{31}P nmr spectrum done by Dr. J. Lancaster, American Cyanamid.

(7) (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) *Bull. Soc. Chim. Fr.*, 2443 (1966); (c) for X-ray evidence confirming P(V) structures, see W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, **87**, 127 (1965).

(8) (a) M. J. Gallagher and I. D. Jenkins, *J. Chem. Soc. C*, 2605 (1969). (b) We disagree with these authors' designation of a minor role to the stabilization of the carbanion end of the 1,3 dipoles. As our evidence indicates, such stabilization is necessary for the reactions of many carbonyl compounds with P(III) species.

(9) For a related discussion see F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967).

SCHEME II



ways depends upon the solvent. Thus **7** rearranges to **11** more in nitromethane than in the less polar methylene chloride, and it mainly reverts to **4** in benzene. The rearrangement of **6** to **10** occurs more readily, even in benzene–hexane upon heating.

In control experiments, **11** was found to be stable to TEP or tributylphosphine (TBP).

Reaction of **6** or **7** with acetonitrile gives the oxazoline **12** (18%) or **13** (54%) as well as the phenanthrones **10** (71%) or **11** (31%) (Scheme II).[10] The oxazoline may form *via* **6** or **7**, or the tetracovalent dipolar form **14**, **15**.[11] This novel formation of a heterocyclic system indicates a synthetic use of pentaoxyphosphoranes which we will investigate further.

Confirmation of the oxazoline structure of **12** was obtained from its mass spectral fragmentation pattern at 75 eV which exhibits major peaks at 385 ($M\cdot^+$), 342 ($M^+ - CH_3CO$), 205 (b), 180 (a), 164 (c), and 152 (d) (Scheme III). Metastable peaks are observed at 304 (calcd for $385^+ \rightarrow 342^+ + CH_3CO$), 131 (calcd for $205^+ \rightarrow 164^+$), 128 (calcd for $180^+ \rightarrow 152^+ + CO$), and 109 (calcd for $385^+ \rightarrow 205^+$). A similar fragmentation pattern is observed for **13** with metastable peaks observed for the processes 2 and 3 (see Experimental Section).

The observed fragmentation of processes 1 and 2 are not compatible with the isomeric isoxazoline [$-ON{=}C(CH_3)-$] structure. The loss of CH_3CO from the molecular ions may actually be occurring from the acetylaziridines **16** and **17** which may form from **12** and **13** upon electron impact. Thermal rearrangement of oxazolines to *N*-acylaziridines have been postulated.[12]

Treatment of **7** with TEP or TBP gives tetrabromobifluorenylidine (**19**, 14,44%) as well as the fluorenone **4** and the phenanthrone **11** (20, 1%). The formation of **19** probably occurs directly from the reaction of **7** with P(III). It may also occur *via* the reversion of **7** to **4** which then reacts with P(III). Evidence against the latter pathway is found in the observation that the reactions of TEP with **3** or **4** give little **18** or **19** (see below).

Other Reactions of Fluorenones with P(III).—The reaction of **3** or **4** with TEP at 150–180 or 100°, respectively, gives the phenanthrone **10** (74%) or **11** (58%), most likely *via* the phosphoranes **6** and **7**. The bifluorenylidines are formed in small yield: **18** (2–3%), **19** (2%). The conversion of **3** to **10** with triisopropyl phosphite has been noted by Poshkus and Herweh.[13] Triphenylphosphine (TPP) gives no reaction with **3** or even with 2,7-dinitrofluorenone (**20**). TBP reacts with **3** or **4** to give **18** or **19**. The highest yields are obtained in neat reaction (44% of **19**) or in benzene (54% of **19**). Treatment of **4** with TBP in toluene or benzene–cyclohexene gives neither **19** nor **11**. The products in these reactions, as exemplified by the benzene–cyclohexene run, are 2,7-dibromofluo-

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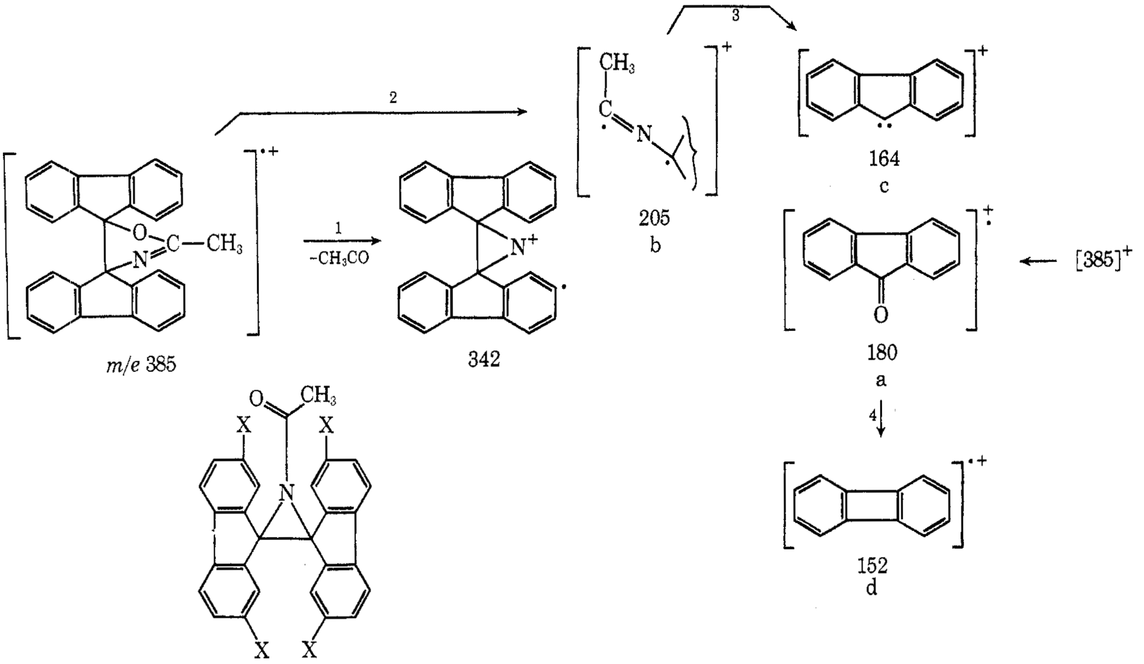
[10] (a) I. J. Borowitz, P. D. Readio, and P. E. Rusek, *Chem. Commun.*, 240 (1968). (b) This work corrects the error in ref 3a.

[11] Alternatively, **6** and **7** may revert to **8** and **9** which react with acetonitrile and then with **3** and **4** as suggested by a referee.

[12] H. L. Wehrmeister, *J. Org. Chem.*, **30**, 664 (1965).

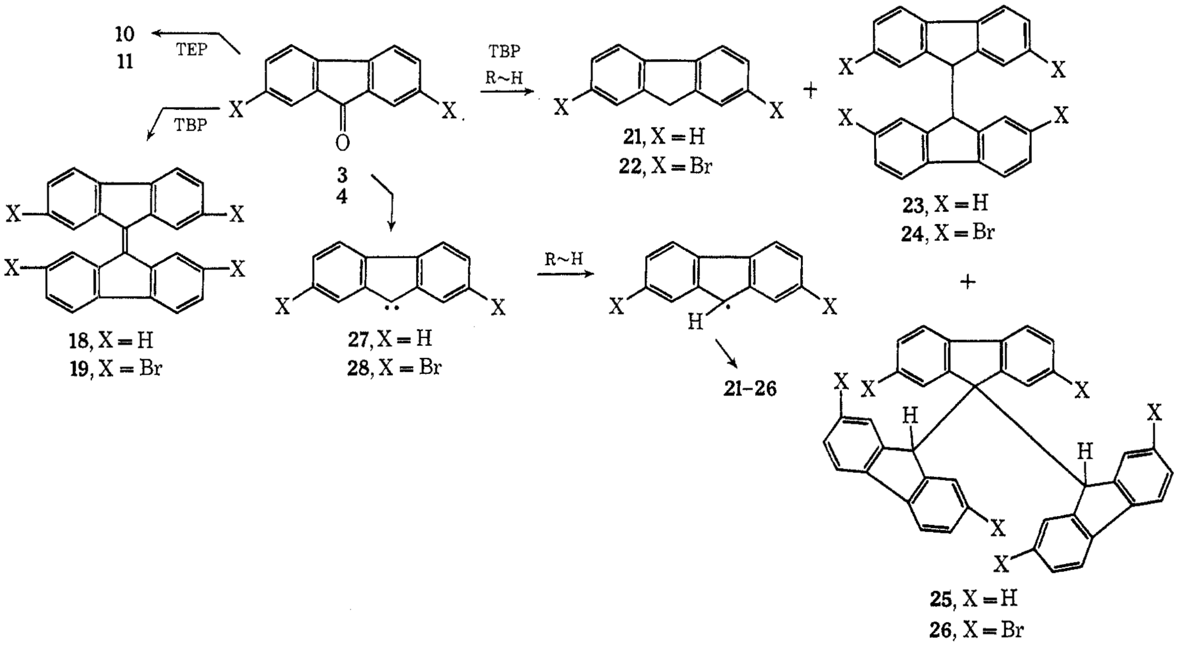
[13] A. C. Poshkus and J. E. Herweh, *ibid.*, **29**, 2567 (1964).

SCHEME III



16, X = H
17, X = Br

SCHEME IV



rene (**22**, 4%), 2,7,2′,7′-tetrabromobifluorenyl (**24**, 0.9%), and 2,7,2′,7′,2″,7″-hexabromotribiphenylenepropane (**26**, 13%) (Scheme IV). The yields are minimal due to isolation and purification difficulties.

Compounds **22** and **24** were identical with genuine samples. The trimer **26** was identical with a genuine sample (melting point, ir and nmr spectrum) kindly supplied by Professor Suzuki.[14] Its mass spectrum was consistent with the assigned structure.[15] Thus the presence of solvents with abstractable hydrogen (the toluene methyl group or cyclohexene) diverts the conversion of **4** from **19** to **22**, **24**, and **26**. These results can be rationalized by the intermediacy of the 2,7-dibromofluorenylcarbene (**28**), which abstracts hydrogen and reacts further. Support for this pathway is found in (a) the photochemical decomposition of 9-diazofluorene (**29**) in the presence of norbornadiene to give the dimer **23** and the trimer **25**[16] and (b) the photochemical conversion of **29** to **23** in the presence of cyclohexane as a hydrogen donor.[17] Our attempts to trap the postulated carbene **28** by cyclopropane formation with acenaphthalene or cyclohexene were

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(14) K. Suzuki, M. Minabe, M. Fujimoto, and N. Nobara, *Bull. Chem. Soc. Jap.*, **42**, 1609 (1969). Genuine **26** was kindly supplied by Professor Suzuki.

(15) High resolution mass spectra of **24** and **26** were done by JEOLCO and by Varian Associates (the latter on an Atlas CH-5 mass spectrometer).

(16) N. Filipescu and J. R. DeMember, *Tetrahedron*, **24**, 5181 (1968).

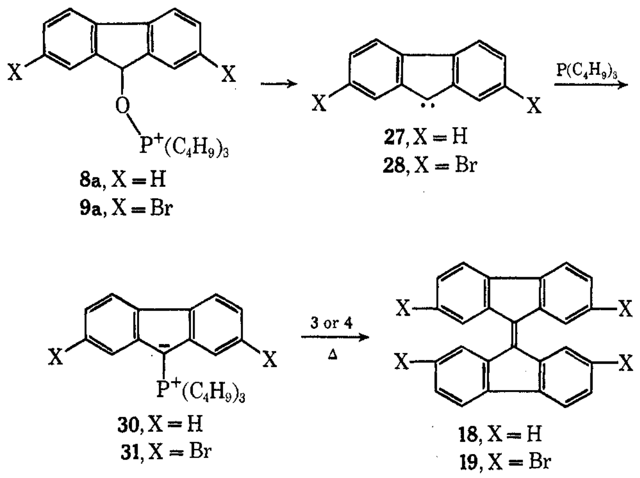
(17) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958).

unsuccessful presumably because the observed products (**19** or **22**, **24**, **26**) were formed more readily.

It is unlikely that **4** is converted to **19** *via* dimerization of the carbene **28** even if it is present. Such dimerizations are rare. Thus while **29** is converted mainly to **18** photochemically,[18] even such reactions may proceed by reaction of diazo compound with carbene.[19]

A reasonable pathway for the formation of **18** or **19** could involve conversion of the 1,3 dipole **8a**, or **9a**, to the carbene **27** or **28** which reacts with TBP to give the ylides **30** or **31**. A Wittig reaction of the ylides **30** or **31** with the fluorenone **3** or **4** would then give **18** or **19**. While the reaction of **30** and **3** does not proceed at low or moderate temperatures,[20] we found that reaction does occur to give **18** (75%) at 145–160°, the approximate temperature range used in our conversion of **3** to **18** with TBP. Thus **18** and **19** may be forming from **3** and **4** by this pathway[21] (Scheme V).

SCHEME V



The Reactions of Tetraphenylcyclopentadienone (1) with P(III) Species.—Our results on the reactions of **1** with P(III) species agree with the pathways postulated for the fluorenone reactions. We had, in the initial phase of our research,[22] found that TPP reacts with **1** at 220–240° to give a $C_{58}H_{40}$ hydrocarbon **32** (54%) which had one allylic hydrogen [nmr ($CDCl_3$) τ 4.79]. The hydrocarbon could not therefore be the initially anticipated octaphenylfulvalene (**33**). Our chemical evidence for the structure of **32** was inconclusive,[22] and we had hoped that an X-ray analysis would solve the problem.[23]

Gallagher and Jenkins have recently found that tris(dimethylamino)phosphine reacts with **1** to give the dipole **34** which when pyrolyzed gives a hydrocarbon which is probably the same as our **32**.[24] They have reasonably postulated the structure to be a benz[*e*]-*as*-indacene (**32**) on the basis of more extensive data then was available to us (Scheme VI). Structure **32** is in full agreement with our spectral and limited degradation data (see Experimental Section). It can be reasonably derived from dipoles such as **34** upon further reaction with the carbene **37**,[8a] or possibly *via* the isomerization of initially formed **33**.[8a, 25]

We have found that TBP reacts with **1** at 100–105° to give **32** (10%) and dihydrooctaphenylfulvalene (**36**, 28%). The latter compound, identical with a genuine sample synthesized from the reaction of 5-bromotetraphenylcyclopentadiene (**39**) with zinc,[26] may arise *via* the intermediacy of the carbene **37** and tetraphenylcyclopentadienyl radical **38** which then dimerizes. Formation of the tetraphenylcyclopentadienyl 5-tributylphosphonium ylide **40** by the pathway possible for the fluorenones is presumably hindered in this case relative to hydrogen abstraction and carbene–dipole reactions, which give **36** and **32**, respectively.[27]

The steric hindrance inherent in the tetraphenylcyclopentadienone system is also reflected in the reported reactions of **1** with trimethyl phosphite[8a] when compared to the fluorenone results. Products arising from internal reactions of the postulated 1:1 dipole were obtained but no 2:1 adduct or its derived products.

As we have already discussed,[3] one of the factors which may influence the formation of bifluorenylidenes and related products from fluorenones by TBP, as opposed to the formation of phosphoranes by TEP, may be the decreased stability of phosphoranes which incorporate a tributylphosphine moiety. Instead the 2:1 adducts may remain in tetracovalent phosphorus "open" forms (related to **14** or **15**) which are in equilibrium with the 1:1 dipole. The 1:1 dipolar adducts can be converted to **18** and **19** as already discussed. The tendency for phosphorus pentacovalency to be favored by electronegative alkoxy groups as found in phosphites has been recently stressed.[9]

Attempted Reaction of Other Ketones with P(III) Species.—In contrast to the substituted cyclopentadienone systems **1**–**4**,[28a] hexafluoroacetone, and trifluoroacetophenone,[4b] other ketones, which cannot form stabilized carbanion oxyphosphonium dipoles, give no reaction with P(III) reagents. The following ketones gave no reaction with TPP, TBP, or TEP under conditions related to those used for **1**, **3**, and **4**: benzophenone,[28b] dibenzo[2,3:6,7]cycloheptanone, xanthone, and benzanthrone (7*H*-benz[*de*]anthracen-7-one).

Mass Spectra of Dihydrofulvalenes.—Tetrabromodifluorenyl (**24**) gave a mass spectral fragmentation pattern shown in Scheme VII.[29]

Metastable peaks were found at 497 (calcd for 646 → 567), 183.5 (calcd for 323 → 244), 161.5 (calcd for 646 → 323), and 109.5 (242 → 163 and 244 → 163), in support of the suggested pathway.

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[18] (a) H. Staudinger and O. Kupfer, *Chem. Ber.*, **44**, 2197 (1911); (b) H. Staudinger and J. Goldstein, *ibid.*, **49**, 1923 (1916).

[19] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 83.

[20] A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960), report that **30** does not react with ketones. Their systems involved reaction temperatures lower than ours, however.

[21] Other pathways are also possible.

[22] M. A. Anschel, Ph.D. Thesis, Lehigh University, 1967.

[23] The hydrocarbon has been submitted for an X-ray analysis to Professor J. White, Fordham University.

[24] Based on similar nmr and uv spectra, melting point data, and chemical behavior.

[25] I. J. Borowitz and P. D. Readio, unpublished observations.

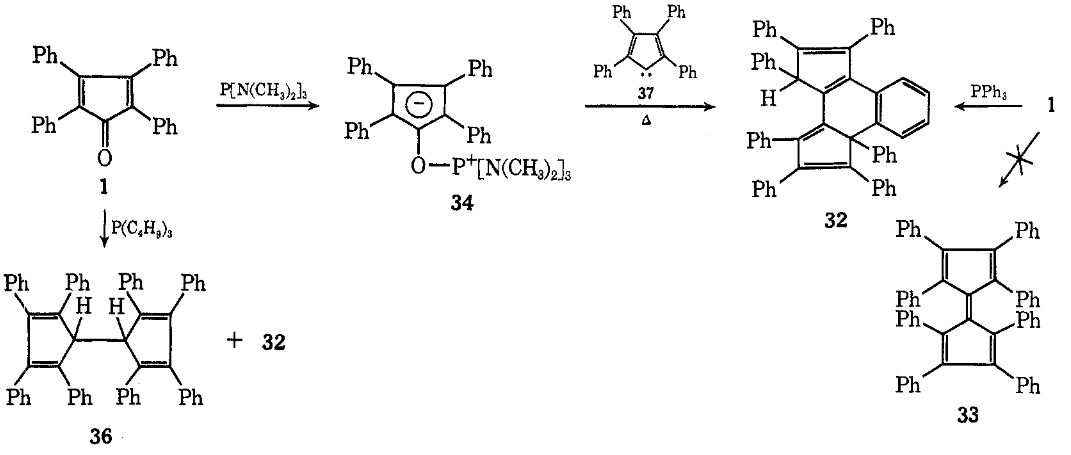
[26] P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 4158 (1961).

[27] Previous attempts to prepare octaphenylfulvalene have failed.[26]

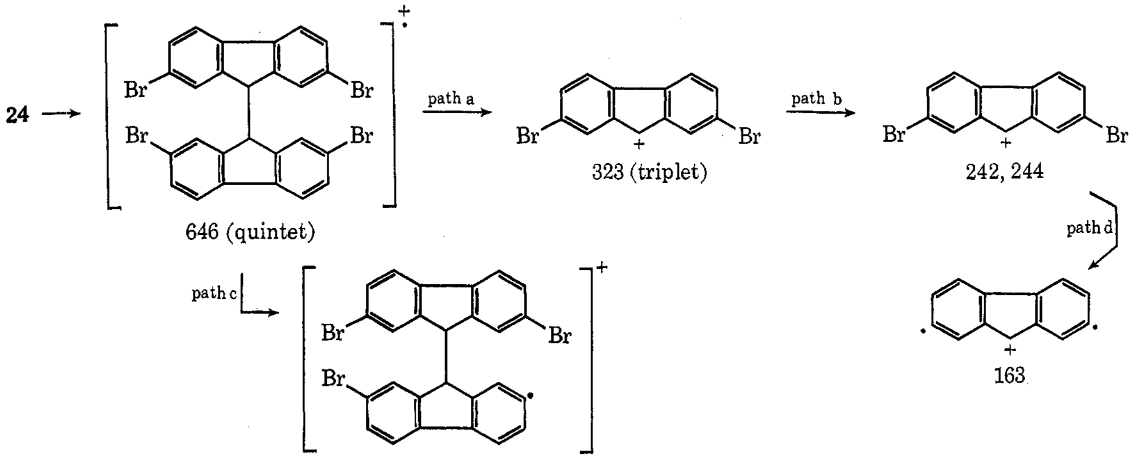
[28] (a) A study of the reactions of 2,3-diphenylindenone with P(III) species will be reported at a later date. (b) Benzophenone reacts with triisopropyl phosphite.[13]

[29] Performed by Mr. David Baugher (Sun Oil), Dr. Jonathan Kurland (Harvard), Dr. Karl Untch (Mellon Institute), and Miss V. Parmakovitch (Columbia) on CEC-103C, MS-9, and Hitachi RMU-6E mass spectrometers.

SCHEME VI



SCHEME VII



Bifluorenyl (**23**) and dihydrooctaphenylfulvalene (**36**) similarly gave abundant M/2 cleavage. In contrast, **32** and the fulvalenes **18** and **19** gave fragmentations with notable absence of M/2 cleavage and the presence of doubly charged ions characteristic of aromatic ring systems.[30]

Experimental Section[31]

All of the solvents used were dried by distillation from phosphorus pentoxide, calcium hydride, or lithium aluminum hydride. Reactions were usually conducted under an atmosphere of dry nitrogen. Organic solutions were dried over magnesium sulfate.

2,7-Dibromofluorenone (4). A. By Bromination of Fluorenone.—A mixture of fluorenone [30.0 g, 0.166 mol; uv max (95% C_2H_5OH) 248, 256.5 nm], bromine (67 g, 0.42 mol), and water (250 ml) was heated at reflux for 24 hr to give an insoluble solid which was washed with aqueous $NaHSO_3$ and dissolved in methylene chloride (*ca.* 1 l.). The resultant solution was dried and cooled to give **4** in several crops (27.8 g, 0.082 mol, 50%): mp 201-202°, lit.[32] mp 202°; tlc (5% EtOAc–C_6H_6) one spot with larger R_f than that of fluorenone; uv max (95% C_2H_5OH) 415 nm; ir (KBr) 5.90 μ.

B. By Oxidation of 2,7-Dibromofluorene.—The bromination of fluorene[33] gave 2,7-dibromofluorene (87%): mp 164°; nmr ($CDCl_3$) τ 2.4, 2.5 (m, 6, aryl H), 6.24 (s, 2, CH_2). Chromic acid oxidation of 2,7-dibromofluorene gave **4** (59%, overall yield 51%), mp 202–203.5°.

2,2,2-Triethoxy-4,5-bisbiphenylene-1,3,2-dioxaphospholane (6).—A mixture of fluorenone (9.8 g, 0.054 mol) and triethyl phosphite (18.6 g, 0.11 mol) was stirred at 25° for 24 hr under nitrogen. Solution of the fluorenone slowly occurred followed by precipitation of **6** which was filtered with suction, washed several times with cold hexane, and dried *in vacuo* to give **6** (8.0–8.65 g, 0.015–0.016 mol, 56–62%): mp 131–135° (sealed tube); ir (KBr) 6.9, 8.3, 8.6, 9.03, 9.6, 10.7 μ; nmr ($CDCl_3$) τ 2.45, 2.97 (m, 16, aryl H), 5.83 (quintet, 6, CH_2, $J_{HH} = J_{PH} = 7$ Hz) and 8.68 (d of t, 9, CH_3, $J_{HH} = 7$ Hz, $J_{PH} = 1.5$ Hz).

Anal. Calcd for $C_{32}H_{31}O_5P$: C, 72.99; H, 5.93; P, 5.88. Found: C, 72.77; H, 5.82; P, 5.64.

The melting behavior of **6** was erratic in that large melting ranges were sometimes observed. This is probably due to the tendency of **6** to rearrange to **10** and triethyl phosphate (see below).

Tetrabromo-2,2,2-triethoxy-4,5-bisbiphenylene-1,3,2-dioxaphospholane (7).—2,7-Dibromofluorenone (**4**, 6.4 g 0.019 mol) was added to triethyl phosphite (9.6 g, 0.058 mol) in methylene chloride (40 ml) with stirring under nitrogen. After 20 min **4** had completely dissolved. After another 20 min acetonitrile (120 ml) was added to give a precipitate which was washed with acetonitrile and dried to give **7** (6.7 g, 0.008 mol, 84%): mp 155–165° (sintering), 197–198°; ir (KBr) 6.90, 7.09, 8.60, 9.64, 10.55, 11.39, 12.34, 12.86, and 13.03 μ; ^{1}H nmr ($CDCl_3$, see Scheme I for proton designations) τ 2.44 (d, 4, H_C, $J_{PH} = 1.5$ Hz), 2.68, 2.81 (d, 4, H_A, $J_{PH} = 1.8$ Hz), 2.94, 3.08 (s, 4, H_B), 5.84 (quintet, $J_{PH} = J_{HH} = 7$ Hz), and 8.62 (d of t, $J_{HH} = 7$ Hz, $J_{PH} = 2$ Hz); ^{31}P nmr ($CDCl_3$) +48 ± 2 ppm (relative to 85% H_3PO_4).[6]

Anal. Calcd for $C_{32}H_{27}O_5Br_4P$: C, 45.64; H, 3.23; Br, 37.96; P, 3.68; mol wt, 842. Found: C, 45.45; H, 3.27; Br, 37.86; P, 3.53; mol wt (osmometric), 836.

Reaction of **4** with TEP in the presence of benzaldehyde or acenaphthalene gave **7** (*ca.* 80%): melting point and nmr spec-

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[30] K. Biemann, "Mass Spectrometry. Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, p 157; see also ref 36, p 49.

[31] The instrumental and other techniques used have been recorded in I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).

[32] J. Schmidt and K. Bauer, *Chem. Ber.*, **38**, 3767 (1905). In the original procedure, recrystallization was done from HOAc.

[33] E. Bergmann and J. Hervey, *Chem. Ber.*, **62**, 909 (1929).

trum identical with genuine **7**. Other products were not isolated. Reaction of **4** with TEP in the presence of acetonitrile for 2 hr also gave **7** (92%); nmr identical with genuine **7**.

Competition of 3 and 4 for TEP.—A mixture of **3** (1.00 g, 0.0056 mol) and **4** (1.90 g, 0.0056 mol) was added to TEP (2.40 g, 0.0144 mol) in methylene chloride (10 ml). The resultant mixture was stirred at 25° for 40 min, and acetonitrile (30 ml) was added to give **7** (1.68 g, 0.0020 mol, 71%). Nmr ($CDCl_3$) was identical with that of genuine **7**. No evidence of other phosphoranes was found.

Reactions of Phosphorane *6*. A. Thermal.—Warming **6** in benzene–hexane gave 9-diphenylenephenanthrone (**10**): mp 262–263°, mmp 262–263° with genuine sample[34] of mp 262–264°; ir (KBr) 5.95, 6.24 μ.

Anal. Calcd for $C_{26}H_{16}O$: C, 90.67; mol wt, 344. Found: C, 90.56; H, 4.79; mol wt (osmometric), 337.

B. Reaction with Acetonitrile to Form Dispiro[fluorene-9,4′-Δ²-2′-methyloxazoline-5′,9′′-fluorene] (12).—Phosphorane **6** (5.0 g, 0.0095 mol) in dry acetonitrile (125 ml) was stirred at 43–46° for 20 hr and cooled to give **10** (1.70 g, 0.0050 mol) and a filtrate which was evaporated *in vacuo* to give a liquid fraction and a solid fraction which was washed with hexane. The liquid fraction and hexane washings were combined to give crude triethyl phosphate (1.54 g; ir, nmr identical with those of a genuine sample). The solid fraction (1.24 g) consisted of **10** (0.61 g, 0.0017 mol) and the oxazoline **12** (0.63 g, 0.0017 mol) as determined by nmr analysis. Total yields follow: **10** (0.0067 mol, 71%) and **12** (18%). A mixture of **10** and **12** was separated by thick layer chromatography (on Brinkman silica gel $PF_{254+366}$ plates) using 5% EtOAc–C_6H_6 to give **10** (R_f 0.53) and **12** [R_f 0.17; mp 249–249.5° (recrystallized from EtOH); ir (KBr) 6.05 μ; nmr ($CDCl_3$) τ 7.45 (s, 3, CH_3) and 2.40 (m, 16, aryl H); mass spectrum (70 eV) *m/e* (rel intensity) 385 ($M\cdot^+$ 1.5), 342 (1.9), 205 (100), 180 (5.6), 164 (58), 163 (19), and 152 (4.3)].

Anal. Calcd for $C_{28}H_{19}NO$: C, 87.23; H, 4.97; N, 3.64. Found: C, 87.48; H, 5.00; N, 3.73.

Reactions of Phosphorane 7. A. Thermal.—Phosphorane **7** (1.82 g, 0.0022 mol) in benzene (20 ml) at reflux for 3.5 hr gave **4** (100%) and triethyl phosphite (tlc).[35] No phenanthrone **11** was formed since it was shown that a maximum of 0.021 g of **11** is soluble in 20 ml of benzene at reflux.

Treatment of **7** with nitromethane at 45–50° for 12 hr or 25° for 20 hr gave phenanthrone **11** (50, 38%), ir identical with that of genuine **11** (see below), and **4** (43, —%). Treatment of **7** with methylene chloride at 25° for 9 days gave **11** (19%).

B. Reaction with Acetonitrile to Form the Tetrabromooxazoline 13.—A suspension of **7** (6.7 g, 0.0080 mol) in dry acetonitrile (140 ml) was stirred at 42–48° for 21 hr to give a light orange colored solid (4.7 g) which contained phenanthrone **11** [1.65 g, 0.0025 mol, 31%; tlc (as above) R_f 0.73] and oxazoline **13** (3.05 g, 0.0044 mol, 54%, R_f 0.50. Yields are based on nmr analysis of the mixture using CH_2Cl_2 as an internal standard. Oxazoline **13**, separated by thick layer chromatography as above, had mp 273–274.5° (recrystallized from C_6H_6); ir (KBr) 6.05, 6.91, 7.08, 7.98, 8.43, 8.54, 9.40, 9.98, 12.40, and 14.82 μ; nmr ($CDCl_3$) τ 2.50–3.02 (m, 12, aryl H) and 7.44 (s, 3, CH_3); mass spectrum[29] (70 eV) *m/e* (rel intensity) 701 center of quintet ($M\cdot^+$, 0.6), 658 center of quintet ($M - CH_3CO$, 0.97), 363 center of triplet ($C_{15}H_9Br_2N$, 100), 338 center of triplet ($C_{13}H_6OBr_2$, 5.5), and 322 center of triplet ($C_{13}H_6Br_2$, 28.7), Metastable peaks were observed at 283, 285.5, and 287.5 (calcd 284, 285.6, and 287.6 for 361, 363, and 365 → 320, 322, and 324), and 180, 182, and 184 (calcd 187 for 701 → 363). The triplets ($n - 2, n, n + 2$) and quintets ($n - 4, n - 2, \ldots, n + 4$) are due to the presence of ^{79}Br and ^{81}Br isotopes.[36]

C. Reaction with Tributylphosphine.—Reaction of **7** (1.42 g, 0.00169 mol) and TBP (0.72 g, 0.0036 mol) without solvent at a bath temperature of 102° with stirring for 1 hr gave, after addition of acetone for fluidity, (a) a red solid which consisted of **7** (0.40 g, 0.00048 mol, 28% recovered, $CHCl_3$ soluble) and 2,7,-2′,7′-tetrabromobifluorenylidene (**19**, 0.16 g, 0.00025 mol, 15%), mp 452–453°, red solid (see below); and (b) a green filtrate which contained **4** (melting point, tlc) among other products. A similar reaction with TBP in greater excess (6.8 equiv) gave **19** (44%) and a small amount of phenanthrone **11** (*ca.* 1%). Reaction of **7** with TBP (6.0 equiv) in benzene at reflux for 49 hr gave **19** (11%) and 2,7-dibromofluorene (**22**, 8%): mp 165–167°, mmp 163.5–165° with genuine **22** of mp 163.5–165.5°.

D. Reaction with Triethyl Phosphite.—Reaction of **7** (1.56 g, 0.00186 mol) with TEP (2.33 g, 0.014 mol) at 100° (bath temperature) for 6 hr gave **19** (0.116 g, 0.00026 mol, 14%), **4** (0.75 g, 0.00022 mol, 3%), and **11** (0.24 g, 0.0036 mol, 20%): melting point, tlc, and ir spectrum identical with those of a genuine sample.

E. Reaction with Triphenylphosphine.—Phosphorane **7** (0.842 g, 0.001 mol) and TPP (1.05 g, 0.004 mol) in toluene (14 ml) were heated at reflux for 24 hr. The resultant mixture contained 2,7-dibromofluorenone (uv) and no **19** (uv).

Reaction of Fluorenone with Triethyl Phosphite.—A mixture of fluorenone (**3**, 2.46 g, 0.0136 mol) and TEP (4.65 g, 0.028 mol) was heated at 150–180° (bath temperature) for 38 hr (**3** left) and another 27 hr to give **10** (1.74 g, 0.0051 mol, 74%): mp 262–263°, mmp 262–263° with genuine sample (see above).

Anal. Calcd for $C_{26}H_{16}O$: C, 90.67; H, 4.69. Found: C, 90.79; H, 4.64.

Phenanthrone **10** was mainly obtained as a C_6H_6-insoluble fraction. The filtrate was chromatographed on silicic acid (45 g, 390 × 20 mm column) to give **18** (0.14 g, 0.00043 mol, 6%): red solid; tlc (5% EtOAc–C_6H_6) R_f 0.86 as for genuine **18** and an impurity of R_f 0.68. The melting points of **18** thus obtained and of **18** prepared from the reaction of 9-bromofluorene with potassium *tert*-butoxide[37] were low (165–179°) when compared with lit.[37] mp 187–189°. Tlc and uv spectral data of our **18** were identical with those of genuine samples.[37,38]

Mass Spectra of Bifluorenylidene (18) and Bifluorenyl (23).—The mass spectrum of **18** (70 eV) had *m/e* (rel intensity) 328 ($M\cdot^+$, 100), 181 (41.5), 164 (11), 77 (18), and 76 (16), while that of **23** had 330 ($M\cdot^+$, 9), 165 (M/2, 100), 163 (4), 139 (2), 115 (1), 77 (0.3), and 76 (0.3).[29]

Reaction of 2,7-Dibromofluorenone with TEP.—A mixture of **4** (3.24 g, 0.0096 mol) and TEP (4.65 g, 0.028 mol) was heated at 100° (bath temperature) for 6 hr with stirring to give an orange solid which was filtered and washed with hot benzene, cold CH_3CN, and cold EtOAc to give the phenanthrone **11** (1.84 g, 0.0028 mol, 58%): mp 391–392° dec; ir (KBr) 5.95 μ; mass spectrum (70 eV) *m/e* (rel intensity, center of multiplets) 660 (M^+, 42), 632 ($M - CO$, 0.4), 579, 581 ($M - Br$, 7), 550 ($M - 2\,Br$, 0.2), 471 ($M - 2Br - CO$, 0.4), 419, 421 ($M - 3Br$, 3.5), 338 ($M - 4Br$, $M - C_{13}H_6Br_2$, 100), 310 ($338 - CO$, 13).[39]

Anal. Calcd for $C_{26}H_{12}OBr_4$: C, 47.34; H, 1.83; Br, 48.46. Found: C, 47.17; H, 2.05; Br, 48.55.

Control Experiments with Phenanthrone 11.—Attempted reaction of **11** with TEP for 24 hr at 100°, or with TBP for 6 hr at 105–110°, gave only recovered **11** and no trace of **19** or other products (tlc).

Attempted Reactions of Triphenylphosphine with Fluorenones.—Treatment of fluorenone (**3**) with TPP in xylene at reflux for 38 hr gave the starting compounds in 98 and 97% yields, respectively, and minor amounts of triphenylphosphine oxide and three unidentified compounds (tlc). Neat reaction of **3** with TPP at 150–160° (bath temperature) for 38 hr similarly gave starting compounds and a trace of **18**. Similar treatment of 2,7-dinitrofluorenone with TPP at 85° for 1.3 hr gave only starting compounds.

Reaction of Fluorenone with Tributylphosphine.—A mixture of **3** (2.46 g, 0.0136 mol) and TBP (5.67 g, 0.028 mol) was heated (bath temperature of 155–165°) for 76 hr with stirring to give a dark red solution which was chromatographed on acid-washed alumina (205 g) to give bifluorenylidene (**18**, 0.883 g, 0.0027 mol, 40%) upon benzene elution. No **10** was obtained.

Reactions of 2,7-Dibromofluorenone with Tributylphosphine. A. Neat.—A mixture of **4** (3.24 g, 0.0096 mol) and TBP (5.67 g, 0.028 mol) was heated at 100° (bath temperature) for 4 hr with stirring to give a dark red solid which was washed with benzene and ethanol to give 2,7,2′,7′-tetrabromobifluorenylidene (**19**, 1.36 g, 0.0021 mol, 44%): mp 454–455° (red needles from bromobenzene) (lit.[40] mp >370°); ir (KBr) 6.9, 7.15, 8.55, 9.15, 9.9, 11.2, 11.5, and 12.4 μ.

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(34) A genuine sample of **10** was kindly provided by Dr. A. Poshkus.[13]

(35) The originally claimed rearrangement of **7** to **11** *under these conditions*[3a,22] was not repeatable.

(36) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966, p 20.

(37) P. M. G. Bavin, *Can. J. Chem.*, **38**, 882 (1960).

(38) Genuine **18** was kindly provided by Professor E. Bergmann (Jerusalem).

(39) Performed by J. Landis on an Atlas CH-5.

(40) L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, **68**, 2014 (1946).

Anal. Calcd for $C_{26}H_{12}Br_4$: C, 48.46; H, 1.86; Br, 49.68. Found: C, 48.23; H, 1.75; Br, 49.45.

The combined filtrate and washings contained at least seven compounds (tlc).

B. In Benzene.—Reaction of **4** (2.00 g, 0.0059 mol) and TBP (6 ml, 4.86 g, 0.024 mol) in benzene (10 ml) at reflux for 69 hr gave crude **19** (1.08 g, *ca.* 54%): mp 450–451° (from bromobenzene); ir as for genuine **19** (see above) but with impurities. The filtrate contained **26** (by ir, see below) and other compounds.

C. In Acetonitrile.—Reaction of **4** (1.62 g, 0.0048 mol) and TBP (2.88 g, 0.014 mol) in dry acetonitrile (distilled from CaH_2 and P_2O_5) at reflux for 2 hr gave **19** (0.371 g, 0.00058 mol, 24%) and **2,7-dibromofluorene** (**22**, 0.667 g, 0.0021 mol, 43%): mp 165.5–166.5° (from C_6H_6), no depression in mixture melting point with genuine sample (see above); ir identical with genuine ir spectrum, Sadtler I.R. Tables, Spectrum No. 25066.

Anal. Calcd for $C_{13}H_8Br_2$: C, 48.19; H, 2.49; Br, 49.32. Found: C, 48.12; H, 2.47; Br, 49.13.

Similar reaction of **4** and TBP in acetonitrile–water (15:1 ml) gave **22** (20%) and **24** (5%) but no **19**. Tetrabromobifluorenyl (**24**), mp 333–337°, had an ir spectrum identical with that of a genuine sample (see below).

D. In Benzene–Cyclohexene.—A mixture of **4** (2.00 g, 0.00592 mol) and TBP (6.0 ml, 4.86 g, 0.0239 mol) in benzene (10 ml)–cyclohexene (10 ml) was heated at reflux for 51 hr to give a solid fraction and a green filtrate. The filtrate was distilled to give benzene and cyclohexene as the only low-boiling components, tributylphosphine, bp 54–59° (0.05 mm), and a residue which gave further solid identical with the above solid fraction. This solid was identified as **2,7,2′,7′,2′′,7′′-hexabromotribiphenylenepropane** (**26**), 0.239 g, 0.000247 mol, 13%: mp 338° dec; nmr (CS_2, 49 accumulations on a Varian C-1024 "CAT") τ 1.29 (s, 2), 2.00 (m, 4), 2.50 (m, 8), 3.46 (s, 2), 4.34 (s, 2), and 4.68 (s, 2); ir (KBr) 6.30, 6.40, 6.95, 7.95, 8.65, 9.4, 12.4, and 12.7 μ; mass spectrum (70 eV) *m/e* (rel intensity, center of multiplets) 962, 964, 966, 968, 970, 972, 974 ($M^{\cdot +}$, $C_{39}H_{20}Br_6$, 7.8), 887 ($C_{39}H_{20}Br_5$, 0.7), 808 ($C_{39}H_{20}Br_4$, 1.4), 725, 727, 729, 731 ($C_{39}H_{20}Br_3$, 2.6), 641, 643, 645, 647, 649 ($C_{26}H_{13}Br_4$, 70), 562, 564, 566, 568 ($C_{26}H_{13}Br_3$, 100), 483, 485, 487 ($C_{26}H_{13}Br_2$, 23), 404, 406 ($C_{26}H_{13}Br$, 78), 321, 323, 325 ($C_{13}H_7Br_2$, 41), 242, 244 ($C_{13}H_7Br$, 15), 162 ($C_{13}H_6$, 13), and 161 ($C_{13}H_5$, 15).[15]

A genuine sample of **26**[14] gave identical nmr and ir (KBr) spectra with the above sample: mp 333° dec, mmp 335° dec.

Anal. Calcd for $C_{39}H_{20}Br_6$: C, 48.39; H, 2.08; Br, 49.53. Found C, 48.23; H, 2.28.

The residue from the green filtrate also gave **22** (0.075 g, 0.000232 mol, 4%) and **24** (0.017 g, 0.000026 mol, 0.9%): mp 315–328° upon crystallization from C_2H_5OH and $CHCl_3$; ir (KBr) identical with genuine **24** ir. No evidence for species such as bicyclohexenyl or other cyclohexene derived compounds was obtained.

Synthesis of 2,7,2′,7′-Tetrabromobifluorenyl (24). A. 2,7,9-Tribromofluorene (41).—A mixture of 2,7-dibromofluorene (**22**, 3.24 g, 0.0100 mol) and *N*-bromosuccinimide (1.78 g, 0.0100 mol) in CCl_4 (50 ml) was stirred and irradiated with a 100-W clear incandescent light bulb for 18.5 hr to give **41** (1.78 g, 0.0044 mol, 44%): mp 196–198° (from glyme); nmr ($CDCl_3$) τ 2.2–2.7 (m, 6, aryl H) and 4.07 (s, 1, methine H).

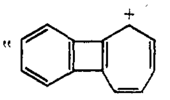
B. Reaction of 41 with Zinc.—A mixture of **41** (1.21 g, 0.00300 mol) and zinc powder (4.50 g, 0.0690 g-atom) in benzene (70 ml) was stirred and heated at reflux for 48 hr to give a mixture which was filtered to give a filtrate from which was obtained **24** (0.45 g, 0.00070 mol, 46%): mp 331–335°; ir (KBr) 6.22, 6.33, 6.9, 7.05 7.15, 8.62, 9.92, 14.2, 15.1 μ; nmr (CS_2, 81 accumulations on CAT) τ 2.55, 2.8 (m, 12, aryl H) and 5.22 (s, 2); mass spectrum[15] (75 eV) *m/e* (rel intensity) 650 (2.4), 648 (8.7), 646 (13.5), 644 (9.7), 642 (2.8), 569 (0.5), 567 (1.3), 565 (1.4), 563 (0.5) 488 (0.5), 486 (1.2), 484 (0.8), 325 (51.6), 323 (100), 321 (52.8), 244 (15.2), 242 (14.9), 163 (62.7), and 150 (4.4). Calcd for $C_{26}H_{14}{}^{81}Br_3{}^{79}Br$: 647.7769. Found: 647.7763.[41]

Anal. Calcd for $C_{26}H_{14}Br_4$: C, 48.34; H, 2.18; Br, 49.48. Found: C, 48.44; H, 2.20.

Reaction of Ylide 30 with Fluorenone.—9-Fluorenyl tributylphosphonium bromide (75% from 9-bromofluorene and TBP[20]), mp 196–198°, lit.[20] mp 194–195°), was converted with aqueous NaOH to ylide **30** (72%, yellow solid), mp 121–122° (lit.[20] mp 123–124°). Reaction of **30** (0.890 g, 0.00230 mol) and **3** (0.414 g, 0.00230 mol) at 145–160° for 24 hr gave a dark red oil which contained tributylphosphine oxide, **3**, and **18** by tlc. Chromatography of the oil on neutral alumina (200 g) gave, upon benzene elution, **18** (0.564 g, 0.00172 mol, 75%) uv spectrum and tlc R_f identical with genuine sample.

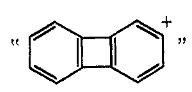
Attempted reaction of **30** with **3** in dry benzene at reflux for 19 hr gave a three-component mixture (by tlc) which contained no **18**.

Reaction of Tetraphenylcyclopentadienone (1) with Triphenylphosphine.—A mixture of **1** (2.0 g, 0.0052 mol) and TPP (3.2 g, 0.012 mol) was kept at 220–240° for 98 hr, dissolved in benzene (10 ml), and then chromatographed on acid washed alumina (566 g). Elution with benzene gave, in the initial fractions, gray-white solid $C_{58}H_{40}$ hydrocarbon (probably **32**,[8a] 1.03 g, 0.0014 mol, 54%), mp 325–326.5° (from acetonitrile). Other runs gave this hydrocarbon, triphenylphosphine oxide, and unreacted starting compounds as the only compounds present by tlc analysis. Longer reaction time and a greater excess of TPP did not improve the yield of **32**: ir (KBr) 3.4, 6.24, 6.9, 7.25, 9.3, 9.7, 13.15, and 14.30 (monosubstituted benzene ring[42]), and 13.30 μ (1,2-disubstituted benzene ring[42]); nmr[43] ($CDCl_3$) τ 2.3–2.8 (m, 10), 2.8–2.9 (m, 5), 2.9–3.05 (m, 5), 3.05–3.2 (m, 10), 3.2–3.5 (m, 4), 3.5–3.7 (d of d, 2), 3.7–3.95 (t of d, 3) and 4.79 (s, 1, benzylic H); uv max (CH_3CN) 235 nm (log ϵ 4.65), 255 (4.59) and 363.5 (4.16); mass spectrum[44] (70 eV) *m/e* (assignment) 736 ($M^{\cdot +}$), 737 (M + 1, 64% of M, calcd 63%), 659 ($M - C_6H_5$), 582 ($M - 2C_6H_5$), 567, 505 ($M - 3C_6H_5$), 504, 491, 428 ($M - 4C_6H_5$), 413, 368 (M^{2+}), 351 ($M - 5C_6H_5$), 274 ($M - 6C_6H_5$), 251, 178 ("$C_6H_5C{\equiv}CC_6H_5$"), 165 (e), 152 (f), 91, and 77.



165

e



152

f

Anal. Calcd for $C_{58}H_{40}$: C, 94.53; H, 5.47. Found: C, 94.59; H, 5.28.

Reactions of the $C_{58}H_{40}$ Hydrocarbon.—The hydrocarbon in solution ($CHCl_3$) was sensitive to oxygen; the ir spectrum changed with time to slowly give C=O peaks at 5.75 and 5.95 μ. Reaction of the hydrocarbon with *N*-bromosuccinimide (3.6 equiv) in CCl_4 under reflux for 95 hr gave a **monobromo derivative** (**42**), mp 185–187°.

Anal. Calcd for $C_{58}H_{39}Br$: C, 85.39; H, 4.82; Br, 9.79. Found: C, 85.44; H, 4.94; Br, 9.66.

Oxidation of a suspension of the $C_{58}H_{40}$ hydrocarbon with 50% aqueous HNO_3 at reflux for 3.5 days gave a clear yellow solution from which was isolated *p*-nitrobenzoic acid (1.8 equiv based on structure **32** which has seven phenyl groups): mp 237–238°; mixture melting point, tlc, and ir spectrum in agreement with genuine sample. Similar oxidation of tetraphenylcyclopentadiene gave 3.1 equiv of *p*-nitrobenzoic acid. Other oxidations (ozone, $KMnO_4$, and O_2) of **32** gave complex mixtures.

Reaction of Tetraphenylcyclopentadienone with TBP.—A slurry of **1** (5.3 g, 0.014 mol) and TBP (5.66 g, 0.0278 mol) was stirred at 100–105° for 24 hr to leave a black solid which was triturated with hot acetonitrile to give the $C_{58}H_{40}$ hydrocarbon (0.526 g, 0.00072 mol, 10%): mp 325–327° (from $CHCl_3$–hexane), mmp 323–326.5° with genuine hydrocarbon (see above) of mp 323–327°. The filtrate of the original trituration gave **dihydrooctaphenylfulvalene** (**36**, 1.43 g, 0.0019 mol, 28% crude): mp 197–200° (from C_2H_5OH), mmp 196–200° with genuine sample (see below) of mp 196–200°; nmr ($CDCl_3$) τ 2.45–3.30 (m, 40, phenyl H) and 4.98 (s, 2 benzylic H); mass spectrum[29,41] (70 eV) *m/e* (rel intensity) 739 (64), 738 ($M^{+\cdot}$, 100), 369 (M/2, 64), 292 (M/2 − Ph), 291 (67), 267 (Ph_3C_3, 8), 191 (Ph_2C_3H, 29), 178 ("PhC≡CPh," 6), 91 (29), 77 (4). Metastable peaks were observed at 230 (calcd for 369 → 292), 185 (calcd for 738 → 369), and 99 (calcd for 369 → 191).

Anal. Calcd for $C_{58}H_{42}$: C, 94.28; H, 5.72. Found: C, 94.55; H, 5.63.

Dihydrooctaphenylfulvalene (**36**).—Reaction of 5-bromo-1,2,3,4-cyclopentadiene (33% from the reaction of *N*-bromosuc-

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[41] Performed by F. Abramson on a CEC 21-492.

[42] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 107.

[43] Performed by E. A. Pier of Varian Associates on an HA-100 nmr spectrometer.

[44] Performed by Professor Klaus Biemann (M.I.T.) and Professor Carl Djerassi (Stanford).

cinimide with tetraphenylcyclopentadiene)[26] with zinc (20 equiv) in benzene at reflux for 24 hr gave **36** (21–34%):[26] mp 197–199°; spectral and melting point data agreed with the data presented for **36** obtained from **1** (see above).

Registry No.—**6**, 14935-22-9; **7**, 15071-25-7; **10**, 1749-36-6; **11**, 27192-88-7; **12**, 19968-81-1; **13**, 19968-82-2; **18**, 746-47-4; **19**, 27192-91-2; **22**, 16433-88-8; **23**, 1530-12-7; **24**, 27192-94-5; **26**, 27192-95-6; **32**, 26307-13-1; **36**, 26307-16-4; **46**, 27250-99-3.

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Electron Spin Resonance Studies of Substituent Effects. IV.[1] Nitroxide Radicals from Bis(*N*-arylnaphthylamines)

ROBERT F. BRIDGER*[2a] AND E. THOMAS STROM[2b]

Mobil Research and Development Corporation, Central Research Division Laboratory, Princeton, New Jersey 08540, and Field Research Laboratory, Dallas, Texas 75221

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Oxidation of bis(*N*-arylnaphthylamines) produces stable nitroxide radicals if the reactive naphthalene positions are blocked. Hyperfine splitting constants and substituent effects are reported and compared with analogous systems. The nitrogen hyperfine splitting in the β derivative is larger than that found in the α derivative. McLachlan molecular orbital calculations are carried out on *N*-phenyl-1-naphthyl nitroxide, *N*-phenyl-2-naphthyl nitroxide, and di-2-naphthyl nitroxide. The nitroxide radicals from these oxidative dimers may be responsible in part for electron spin resonance signals obtained during oxidation of aromatic amines such as *N*-phenyl-1- and *N*-phenyl-2-naphthylamine.

While various derivatives of phenyl nitroxides and diphenyl nitroxides have been studied in detail by electron spin resonance (esr),[3–6] no convincing spectra of *N*-arylnaphthyl nitroxides have appeared in the literature. Hoskins[7] reported spectra generated from aromatic amines added to base-catalyzed autoxidations of toluene–alcohol mixtures. Although the spectrum of diphenyl nitroxide was generated from diphenylamine, the spectrum produced from *N*-phenyl-2-naphthylamine did not exhibit the expected nitrogen hyperfine splitting constant (hfsc) and was quite narrow, suggesting a possible semiquinone radical arising from the oxidation products of *N*-phenyl-2-naphthylamine.[8]

Buchachenko[9] has reported spectra assigned to *N*-phenyl-1- and *N*-phenyl-2-naphthyl nitroxides. The 1-naphthyl derivative exhibited, in addition to a 10.8-G nitrogen hfs, a 2.4-G hfs characteristic of the ortho and para protons of the phenyl group, but no mention is made of the relatively large hfs expected of the 2- and 4-naphthyl protons. The 2-naphthyl derivative gave a gross triplet of 9.5 G with fine lines discernible on the main pattern. In their excellent review,[4] Forrester, Hay, and Thomson briefly refer to unpublished work on *tert*-butyl-1- and *tert*-butyl-2-naphthyl nitroxides, but no spectra are given. They note A^N's for these nitroxides are 13.5 and 11.75 G, respectively, for the α- and β-naphthyl derivatives.

Several recent studies[8,10] of the *N*-phenyl-2-naphthylamino radical reveal that its chemistry is dominated by the high reactivity at the 1 carbon, resulting in coupling products when generated by oxidation of the amine or thermolysis of the tetrazene,[10] and mixtures of quinoid products when generated by reaction of the amine with peroxy radicals in the presence of hydroperoxide.[8,11] These results suggest that many routes to *N*-arylnaphthyl nitroxides will be diverted to other products. Since the oxidative dimers may be responsible in part for esr signals observed on oxidation of *N*-arylnaphthylamines, an investigation of the nitroxide radicals of these dimers should be instructive. The present paper deals with nitroxides derived from oxidation products of *N*-phenyl-1- and *N*-phenyl-2-naphthylamine.

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[1] (a) Part III: E. T. Strom and J. R. Norton, *J. Amer. Chem. Soc.*, **92**, 2327 (1970); (b) presented in part at the Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970.

[2] (a) Author to whom inquiries should be addressed at the Central Research Laboratory; (b) Field Research Laboratory.

[3] E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, **32**, 3853 (1967).

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