This solid is insoluble in benzene, carbon tetrachloride, and chloroform and is assumed to be a low molecular weight polymer containing chlorine.

Ionic Reaction of Iodobenzene Dichloride[8] with Cyclodecenes. —For 10 min oxygen was admitted through a sintered-glass dispersion tube and bubbled into a solution of cyclodecene (0.05 mol) in carbon tetrachloride (30 ml), iodobenzene dichloride (0.05 mol) was added to the solution, and the oxygen flow was continued until the insoluble iodobenzene dichloride had disappeared (approximately 36 hr). Hydrogen chloride was evolved during the reaction. The solvent was removed by rotary evaporation, the product mixture was distilled at reduced pressure, and the distillate fractions were examined by ir and nmr techniques. Table I summarizes the product distribution data. Some of the distillate fractions were mixtures; a low-boiling fraction contained isomeric chloroiodobenzenes[8] as well as 3-chloro-1-cyclodecene, and the dichlorocyclodecane fraction from *cis*-cyclodecene was a mixture of vicinal and transannular dichlorides.[13] These mixtures were not separated satisfactorily, but they were readily analyzed by nmr spectroscopy.

Radical Reaction of Iodobenzene Dichloride[8] with Cyclodecenes. —A mixture of cyclodecene (0.05 mol), carbon tetrachloride (30 ml), and iodobenzene dichloride (0.05 mol), contained in a 100-ml round-bottom flask, was degassed by a freeze-thaw method to eliminate molecular oxygen. The flask was sealed, and the mixture was stirred with a magnetic stirrer at room temperature until the iodobenzene dichloride had disappeared (5 hr). Hydrogen chloride was evolved when the flask was opened. The mixture was worked up as described above for the ionic reaction with iodobenzene dichloride. The nmr spectrum of the dichlorocyclodecane fraction indicated that only transannular dichlorides were present.[13]

Reaction with *trans*-cyclodecene (but not with *cis*-cyclodecene) led to the formation of 1.3 g of a white, flocculant solid, which recrystallized from chloroform–methanol as needles which did not melt below 330°. This solid was not examined further.

Product Identification. 3-Chloro-1-cyclodecene distilled at 51-55° (0.15 mm): nmr (DCCl₃) −5.50 (2 H, C=CH), −4.21 (1 H, HCCl), −2.05 (4 H, CH₂CCl and CH₂C=C), and −1.43 (10 H, CH₂CH₂CH₂), all multiplets. *Anal.* Calcd for C₁₀H₁₇Cl: C, 69.55; H, 9.92. Found: C, 69.42; H, 10.02. The stereochemistry of the C=C was not determined.

The addition product identified as *trans*-1,2-dichlorocyclodecane, bp 68–72° (0.17 mm), gave an nmr spectrum (DCCl₃) consistent only with a 1,2 isomer:[4a] −4.36 (2 H, HCCl), −2.08 (4 H, HCCCl), and −1.57 (12 H, CH₂CH₂CH₂), all multiplets. The signal at −4.36 was a broad, complex one from which coupling constants could not be discerned, even with decoupling experiments. Partial dehalogenation of a sample of the dichloride with zinc dust in refluxing ethanol, and partial dehydrochlorination by potassium *t*-butoxide in dimethyl sulfoxide solution (room temperature), produced olefin (78% *trans*- and 22% *cis*-cyclodecene from zinc reaction; 1-chloro-1-cyclodecene from potassium *t*-butoxide reaction) and left dichloride whose nmr spectrum was unchanged from that of the starting material. Since the isomeric *cis*- and *trans*-1,2-dichlorocyclodecanes are expected to undergo these elimination reactions at different rates, these results are taken to be strong evidence that a single 1,2-dichloride was formed in the addition reaction. Since *cis*-1,2-dichlorocyclodecane (synthesized by refluxing a mixture of *cis*-diol, excess thionyl chloride, and dioxane[14]) is a solid [mp 84.5–86.5°; nmr (DCCl₃) −4.96 (HCCl)], the addition product is *trans*-1,2-dichlorocyclodecane.

trans-1,6-Dichlorocyclodecane (mp 101–103°) crystallized from a distillation fraction [bp 63–66° (0.10 mm)] from some of the chlorine additions. The nmr spectrum (DCCl₃) reveals an A:B:X proton ratio of 8:8:2, consistent with a 1,4-, 1,5-, or 1,6-dichloride structure.[4a] A portion of the dichloride was converted into *trans*-1,6-bis(phenylthio)cyclodecane,[4d] mp 101–103° (mixture of *trans*-1,6-dichloro- and *trans*-1,6-bis(phenylthio)cyclodecanes, mp <93°).

Registry No. —*cis*-Cyclodecene, 935-31-9; *trans*-cyclodecene, 2198-20-1; chlorine, 7782-50-5; iodobenzene dichloride, 932-72-9.

(14) D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953).

Reactions of Phosphorus Azides with Activated Alkynes[1]

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Phosphorus azides are known to add to a variety of substituted alkenes,[4–9] but there appears to be no record of studies on the reactions with alkynes, although a few condensations of some alkynes with aryl and alkyl azides have been summarized.[9,10] We wish to report that 1a and the ynamine 2a react in boiling benzene to

$$R_2P(O)N_3 \qquad R'C{\equiv}CR''$$

1a, R = C₆H₅ 2a, R′ = (C₂H₅)₂N; R″ = CH₃
b, R = C₂H₅O b, R′ = C₂H₅O; R″ = H

3
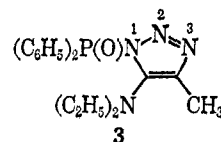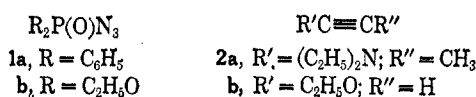
yield crystalline 3 (49%). Infrared (P→O at 8.1 μ) and nmr analyses (Table I) support the structure. Rapid hydrolytic cleavage occurred with 3 upon exposure to the atmosphere to give the triazole 4 and diphenyl-

$$3 \xrightarrow{\text{H}_3\text{O}^+} \quad + \quad (C_6H_5)_2P(O)OH$$

4   5
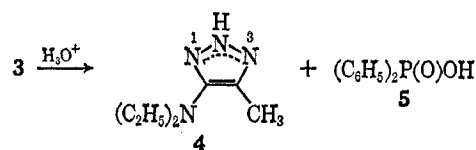
phosphinic acid (5). Acid hydrolysis gives 4 and 5 in near-quantitative yield. The broadness of the signal for the proton on nitrogen in the nmr spectrum (CDCl₃) of 4 suggests tautomers with the hydrogen on N-1 and N-3. Although isomers 3 and 6 are possible from reaction of 1a and 2a, evidence favors 3. Several types of molecular models indicate a strong probability of nonbonded interaction between the (C₆H₅)₂P(O) and (C₂H₅)₂N groups in 3 and between the (C₆H₅)₂P(O) and CH₃ groups in 6, respectively. Restricted rotation around the P–N and C₆H₅–P bonds in 3 and 6 might

(4) K. D. Berlin and L. A. Wilson, *Chem. Ind.* (London), 1522 (1965).
(5) K. D. Berlin and L. A. Wilson, *Chem. Commun.*, 280 (1965).
(6) K. D. Berlin and M. A. R. Khayat, *Tetrahedron*, **22**, 975 (1966); **22**, 987 (1966).
(7) K. D. Berlin, L. A. Wilson, and L. M. Raff, *ibid.*, **23**, 965 (1967).
(8) K. D. Berlin and R. Ranganathan, *ibid.*, **25**, 793 (1969).
(9) F. R. Benson and W. L. Savell, *Chem. Rev.*, **46**, 1 (1950).
(10) R. Huisgen, R. Knorr, L. Möbius, and G. Szeimies, *Chem. Ber.*, **98**, 4014 (1965).

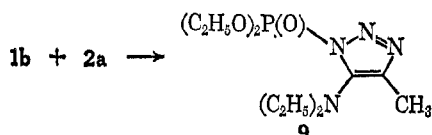TABLE I

60-MHz NMR DATA FOR PRODUCTS IN δ VALUES (*J*, HERTZ)

Compd	CH₃	=CCH₃	CH₂	NH	ArH	CH₃	CH₂OP
3	1.03 t (7)	2.29 s	3.22 q (7)		7.46 m		
4	1.06 t (7)	2.3 s	3.21 q (7)	13.0 m br			
9	0.98 t (7)	2.2 s	3.12 q (7)			1.38 t (7)	4.25 quintet (7)

expectedly be reflected in the chemical shift and shape of nmr signals for protons in the ethyl group of **3** or in the signal for the protons on the methyl group attached to the ring in **6**. Low-temperature studies at 0, −20,
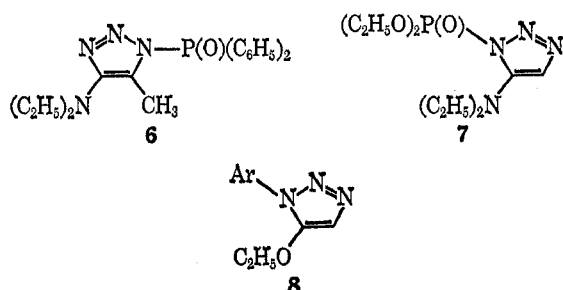

−40, and −60° at 60 and 100 MHz of **3** and **4** in CCl₄ indicate increased broadening of the signals for the protons of the ethyl group, although the effect was more pronounced in **3**. Virtually no change in δ value or shape of the singlet was observable for the methyl group on the ring in **3** or **4**. On this basis **6** is less tenable. Moreover, the mode of addition of **1a** to **2a** appears to be similar to the condensations of *para*-substituted aryl azide with ethoxyacetylene, which yielded **8** in high yield.[10]

Similarly, **1b** and **2a** under identical conditions give a liquid tentatively identified by nmr as **9**, which is thermally unstable and decomposes upon attempted distillation. Chromatography of **9** over neutral alum-


ina led to P–N cleavage. Condensation of **1b** and **2a** in the absence of solvent near room temperature (initial mixing near 0° for 2 hr) gave **9** which, *via* nmr (Table I) examination, appeared to be of high purity. Again, heavy decomposition of **9** ensued when distillation was tried even in a molecular still.

Ethoxyacetylene (**2b**) and **1a** or **1b** react when heated in the absence of solvent under N₂ with heavy tar formation. In benzene, the condensation is sluggish over 3–4 days with recovery of starting azides and the production of tar. Interestingly, **1b** and **2b** combine in a novel but unknown fashion to give triethyl phosphate
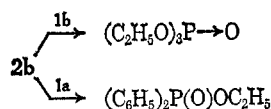
(33%). Likewise, tar and ethyl diphenylphosphinate result from **1a** and **2b**. Both of these data are in contrast to that reported for reaction of **2b** with ArN₃, where a triazole results.[10,11] Whether or not ethoxyla-

(11) P. Grünanger, P. Vita Finzi, and E. Fabbri, *Gazz. Chim. Ital.*, **90**, 413 (1960).

tion of phosphorus to give a POC₂H₅ group is at the expense of **2b** or an intermediate, such as **10**, is not
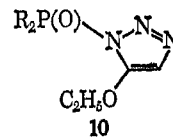
readily discernible, since the reaction mixtures begin to darken quickly when the reagents are heated, apparently an indication of the presence of tar. Glpc analyses of both mixtures indicate very small amounts of several other products (<5% total) and suggest a complex process.

Experimental Section

Reaction of Diphenylphosphinyl Azide (1a) with 2a. Preparation of Triazole 3.—To solution of distilled **2a** (3.35 g, 0.03 mol) [obtained from Fluka AG, Buchs SG, bp 130–132° (760 mm)], in dry benzene (15 ml) was added a solution of **1a**[12] (7.30 g, 0.03 mol) in dry benzene (15 ml) over 30 min at 60–65° in a dry box under N₂. The mixture was then boiled for 3 hr. Cooling to room temperature resulted in a dark brown solution, which was diluted to turbidity with hexane and left overnight, whereupon a white solid separated. The mixture was removed from the dry box and chilled in ice; the filtered solid (5.07 g, 49%) melted at 118–120°. Recrystallization from benzene–petroleum ether gave pure **3**, mp 120.5–121.5°.

Anal. Calcd for C₁₉H₂₃N₄OP: N, 15.81; P, 8.74. Found: N, 15.55; P, 8.74.

Hydrolysis of Triazole 3.—The triazole **3** (354 mg, 1.0 mmol) was stirred at room temperature with 5% HCl (20 ml) for 30 min, and the mixture was poured into saturated NaHCO₃ solution. Ether extracts of the aqueous mixture were dried (MgSO₄) and the solvent was evaporated to give 150 mg (98%) of **4**. Distillation gave **4**, pure by tlc and nmr, bp 60–70° (0.25 mm).

Anal. Calcd for C₇H₁₄N₄: N, 36.33. Found: N, 35.94.

Acidification with dilute HCl of the aqueous mixture precipitated **5** (191 mg, 87%), identified by mixture melting point with an authentic sample.

Reaction of Diethyl Phosphorazidate (1b) with 2a.—To a solution of **2a** (2.22 g, 0.02 mol) in dry benzene (10 ml) over a 1-hr period was added **1b** (3.58 g, 0.02 mol) under N₂. The temperature rose to 44° and fell to 27° within the next 40 min. After another 0.5 hr, the solvent was removed to give 5.5 g of a dark liquid. Distillation at 120–130° (0.005 μ) resulted in extensive decomposition with a black tar produced. After the reactants were mixed and stirred at 0–10° for 2 hr under N₂, the temperature was raised to and maintained at 24–26° for another 2 hr. As in the previous experiment, the absence of the azide band at 4.61 μ in the infrared spectrum of the reaction mixture indicated a high conversion. Nmr analysis of both mixtures prior to attempted distillation was that found in Table I for **9**. Tlc of the mixture before distillation indicated several very minor impurities, and thus an elemental analysis of **9** was precluded.

Reaction of 1b with 2b.—A solution of **1b** (16.3 g, 0.1 mol) and freshly distilled **2b** (7.0 g, 0.1 mol) [obtained from Farchan Research Laboratories, bp 45–50° (749 mm),[13] nmr (neat with trace TMS) δ 1.34 (t, *J* = 7 Hz), 1.47 (s), and 4.06 (q, *J* = 7 Hz)] in benzene (20 ml) was stirred and boiled for 90 hr under N₂. The dark mixture was cooled to room temperature and then distilled Unreacted **1b** (9.0 g, 55%) and triethyl phosphate (6.0 g, 33%) were obtained and compared with authentic samples. Glpc

(12) Azides **1a** and **1b** are described elsewhere.[4–8]

(13) E. R. H. Jones, G. Eglinton, M. D. Whiting, and B. L. Shaw ["Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 404] report a boiling point of 49–51° (749)mm

analysis of the remainder of the product on a 5 ft × 0.125 in. column of 10% Carbowax 20M on 80–100 mesh (DMCS), A-W revealed small amounts (<5% total) of several other products.

Reaction of 1a with 2b.—A solution of 1a (16.9 g, 0.07 mol) and freshly distilled 2b (10.5 g, 0.15 mol) in 25 ml of dry benzene was stirred at reflux for 4 days under N_2. Petroleum ether (bp 40–60°) was added to the mixture at room temperature, causing a black oil to separate with a solid suspended in it. Distillation of the petroleum ether–benzene gave back 4.5 g (27%) of 1a.

The black oil was redissolved in benzene and a small amount of solid precipitated was filtered from solution. Separation and subsequent purification identified the solid as diphenylphosphinic acid. The benzene solution was distilled to give 5.0 g (34.5%) of ethyl diphenylphosphinate (based on 1a), identified by comparison with an authentic sample.[14]

Registry No.—3, 23646-70-0; 4, 23596-01-2; 9, 23646-71-1.

(14) A general procedure for the preparation of alkyl diarylphosphinates is available; see K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *J. Org. Chem.* **30**, 1267 (1965).

Autoxidation of Some Phenols Catalyzed by Ring-Substituted Salcomines

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It has been shown that salcomines (see Table I) catalyze the autoxidation of 2,6-substituted phenols selectively, to give the corresponding benzoquinones (BQ), diphenoquinones (DPQ), or polymers.[1] The selectivity of the salcomine catalysts was correlated, in a qualitative way, with the amounts of the mononuclear salcomine and its O_2-bridged dimer present in solution at equilibrium.

We studied the catalytic oxidation of 2-methyl-6-benzylphenol and 2,6-dichlorophenol using a series of ring-substituted salcomines to see whether the nature of the substituent would affect their selectivity or oxidizing power (the dichlorophenol cannot be oxidized with unsubstituted salcomines).[1] Several *stoichiometric* oxidations of 2-methyl-6-benzylphenol were carried out using the unsubstituted pyr-salcomine and varying the time at which O_2 was admitted to the system.

Experimental Section

Preparation and Properties.—The preparation and properties of all of the salcomines used in this study are described in the literature.[1–3] They are readily obtained in high purity as highly colored, crystalline solids by the reaction in aqueous solution of a cobalt salt, ethylenediamine, and pyridine with the appropriate substituted salicylaldehyde. The elemental analyses (C, H, N, Co, and halogen when present), color, and crystal form of all of the salcomines used in this study were in excellent agreement with those reported in the literature.

Oxidations. Salcomines in Catalytic Amounts.—To a mixture of 0.0005 mol of catalyst (based on the molecular weights shown in Table I) in 100 ml of chloroform was added 0.01 mol of the 2,6-

(1) L. H. Vogt, Jr., J. G. Wirth, and H. L. Finkbeiner, *J. Org. Chem.*, **34**, 273 (1969).

(2) R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1886 (1947).

(3) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963).

substituted phenol. Oxygen was bubbled through the solutions at room temperature for 24 hr. The reaction mixtures were then filtered, diluted to 250 ml with chloroform, and analyzed as described below.

Salcomines in Stoichiometric Amounts.—The catalyst used in these oxidations was bis(salicylaldehyde)ethylenediiminepyridinecobalt(II) (Table I, entry 10), and the phenol used was 2-methyl-6-benzylphenol. Two procedures were followed.

(A) The catalyst (0.005 mol, 2.02 g) was slurried with 140 ml of CHCl$_3$ *under nitrogen*. Then 0.01 or 0.005 mol (1.98 or 0.99 g) of the phenol was added as a solution (flushed with N_2) in 130 ml of CHCl$_3$. The initial red-purple color of the slurry did not change during this time, or for 0.5 hr after the phenol was added. The heterogeneous mixture was then flushed with O_2 and within 5 sec it turned dark brown and became homogeneous. Oxygen was bubbled through the solution for a total of 24 hr, after which it was filtered, made up to 250 ml with CHCl$_3$, and analyzed as described below.

(B) The catalyst (0.005 mol, 2.02 g) was slurried with 140 ml of CHCl$_3$ *under oxygen*. The phenol (0.01 and 0.025 mol) was then added and procedure A was followed from this point on. The mixture was brownish before and after adding the phenol and became homogeneous after adding the phenol.

C. Analytical Methods.—The reaction mixtures were analyzed for products and unreacted 2,6-disubstituted phenols using methods described previously.[1]

A qualitative test for the presence of polymers was made by pipetting a few milliliters of the reaction mixture into 100 ml of methanol. The absence of a precipitate indicated that if any polymers were present they were of very low molecular weight ($[\eta] < ca.$ 0.01 dl/g).

The 2,6-dichlorobenzoquinone could not be isolated by tlc, since it appeared to react with itself on the tlc plates to give an insoluble product. It was necessary to reduce the reaction mixture with zinc-acetic acid, acetylate the corresponding hydroquinone using acetic anhydride, and identify the resulting product from its glpc retention time, mass spectrum, and ir spectrum by comparison with authentic material.

Results and Discussion

The results of the catalytic oxidations of 2-methyl-6-benzylphenol are shown in Table II. A general trend in the conversions and oxidation products was observed in progressing from the more electron-donating groups as substituents on the phenyl rings of the salcomine catalysts to the more electron-withdrawing groups. The donor group favored higher conversions, higher yields of the BQ, and lower yields of the DPQ than the withdrawing groups. A more precise correlation between the nature of the products and the relative strengths of the donating or withdrawing groups is not possible at this time. There were no apparent correlations of the BQ to DPQ ratios with Hammett σ values. If we consider our earlier suggestion[1] that BQ's arise from reaction of the phenols with the O_2-bridged salcomine dimers and DPQ's by reaction with their mononuclear forms (in an equilibrium mixture), then our present data suggest that electron-withdrawing groups shift the equilibrium to favor the mononuclear species and the electron-donating groups favor the binuclear species. This suggestion is supported by inspection of a plot of per cent oxygenation *vs.* O_2 pressure for the 3-methoxy- and 3-nitrosalcomines.[4] At atmospheric pressure the methoxy derivative is more highly oxygenated, *i.e.*, more of it is in the O_2-bridged dimer form, than the 3-nitro derivative.

We considered the possibility that the formation of a BQ or DPQ could be determined by the oxidation potential and/or coordination geometry of either a phenol-

(4) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, pp 346, 347.