of structures and SCF–MO calculations has now been established, and a theoretical explanation is desirable.

The failures of the HMO method to correlate the data reviewed were attributed[12,17] to the lack of consideration of electron repulsion effects in the HMO treatment. If the SC algorithm is justified in future theoretical work, that previous conclusion may require modification. No explicit electronic charge effects are included in a structure–resonance theory that only includes Kekulé resonance structures.

At present, the efficacy of the SC approach has only been demonstrated for alternant π systems, and this may constitute a limit to use of this idea. The extension to nonalternant systems is under investigation.

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Synthesis of Arylphosphonous Dichlorides, Diarylphosphinous Chlorides, and 1,6-Diphosphatriptycene from Elemental Phosphorus

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Reaction of elemental white phosphorus with aryl halides at temperatures ranging from 280 to 350°C in the presence of Lewis acid catalysts gave arylphosphonous dichlorides and diarylphosphinous chlorides. Reaction of white phosphorus with *o*-dichlorobenzene in the presence of $FeCl_3$–$TiCl_4$ produced in addition to *o*-chlorophenylphosphonous and di(*o*-chlorophenyl)phosphinous chloride 1,6-diphosphatriptycene, a novel, phosphorus-containing heterocyclic compound.

The preparation of phenylphosphonous dichloride (**1a**) and diphenylphosphinous chloride (**1b**) has been investigated earlier by several research groups. One of the best routes to **1a** developed previously involved the reaction of benzene with phosphorus trichloride in the presence of aluminum chloride in stoichiometric quantities.[1]

$$C_6H_6 + PCl_3 \xrightarrow{AlCl_3} \underset{\textbf{1a}}{C_6H_5PCl_2} + HCl$$

The resulting phenylphosphonous dichloride (**1a**) forms strong complexes with the aluminum chloride catalyst. The extraction of the product is therefore difficult. An improvement of the isolation procedure was introduced by adding phosphorus oxychloride in stoichiometric quantities as a complexing agent to remove the aluminum chloride.[2,3]

Since phenylphosphonous dichloride (**1a**) disproportionates in the presence of aluminum chloride to yield diphenylphosphinous chloride (**1b**) and phosphorus trichloride[4-6]

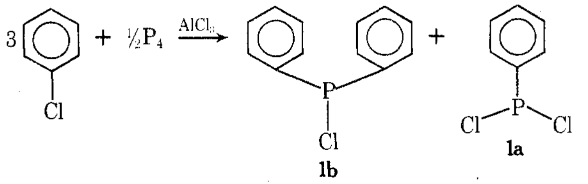
$$\underset{\textbf{1a}}{2C_6H_5PCl_2} \xrightarrow{AlCl_3} \underset{\textbf{1b}}{(C_6H_5)_2PCl} + PCl_3$$

the reaction of benzene with phosphorus trichloride and aluminum chloride may be used to produce diphenylphosphinous chloride directly without isolating phenylphosphonous dichloride. The complex of diphenylphosphinous chloride with aluminum chloride formed during the disproportionation may be split by addition of potassium chloride.[4]

In this paper we wish to report the synthesis of phenylphosphonous dichloride and diphenylphosphinous chloride in high yield by a new and simple method from chlorobenzene and elemental white phosphorus.[7]

Results and Discussion

The subject reaction is carried out by heating elemental phosphorus in an excess of the chlorobenzene in a sealed glass tube at 350°C for several hours. The reaction is catalyzed by small quantities of aluminum chloride or bromide or the corresponding ferric halides.



This method may be employed also for the preparation of substituted arylphosphonous dichlorides and diarylphosphinous chlorides from elemental phosphorus and substituted aryl chlorides.

In a typical experiment the aryl halide (4.0 mol) was heated with elemental white phosphorus (2.2 g-atoms) in the presence of 0.05 mol of anhydrous ferric or aluminum chloride at elevated temperatures for 8 hr. Reactions with *o*- or *p*-dichlorobenzene, *o*-, *m*-, or *p*-chlorotoluene, 1,2,4-trichlorobenzene, or 1-chloronaphthalene gave satisfactory yields when heated at 325°C. The reaction with chlorobenzene required higher temperatures (350°C).

In addition to ferric chloride and aluminum chloride we have found also titanium tetrachloride to be an effective catalyst. The results of these reactions are summarized in Table I.

If the catalyst was allowed to stand in the reaction mixture for several days before the heating was started it became inactive. It seemed that the metal chloride had reacted with the white phosphorus forming a new product (possibly a metal phosphide) which is inactive as catalyst.

In the absence of any catalyst the main reaction taking place under identical conditions was the conversion of white phosphorus into its red modification. In some cases the formation of arylphosphonous dichlorides or diarylphosphinous chlorides occurred, but at a much slower rate than in the presence of a catalyst. In general, only traces of these reaction products were formed.

The reaction of elemental white phosphorus with aryl halides containing nitro groups such as 1-chloro-2-nitrobenzene led to violent reactions which caused the tubes to break. This was probably due to a sudden deoxygenation of the nitro group involving the interaction with phosphorus.

Synthesis of 1,6-Diphosphatriptycene. In an effort to optimize the conditions for the formation of some of these arylphosphonous and arylphosphinic halides we observed that in the reaction of *o*-dichlorobenzene with white phosphorus the composition of the reaction product mixture was strongly influenced by the type of catalyst, reaction time, and temperature. The reaction proceeded smoothly at 325°C in the presence of a small quantity of ferric chloride. In a typical experiment 70 g of white phosphorus, 8 g of ferric chloride, and 585 g of *o*-dichlorobenzene were heated for 7 hr at 325°C in a sealed tube. The resulting reaction mixture was a clear dark liquid which, on distillation, gave 76 g of *o*-chlorophenylphosphonous dichloride (**2a**) and 80 g of di(*o*-chlorophenyl)phosphinous chloride (**2b**).

If ferric chloride was replaced by titanium tetrachloride (see Table II) a much higher yield of compounds **2a** and **2b** was produced. This points out the much greater reactivity of titanium tetrachloride vs. ferric chloride. In addition the formation of a small quantity of crystalline material in the reaction mixture was observed. A combined catalyst of ferric chloride and titanium tetrachloride produced a large quantity of this crystalline substance (**10**) and some liquid material. The liquid material comprised a mixture of the above mentioned *o*-chlorophenylphosphonous dichloride,

Table I[p]
Arylphosphonous Dichlorides and Diarylphosphinous Chlorides from Elemental White Phosphorus and Aryl Halides

Compd	R	Bp, °C (mm)	Mp, °C	% yld
1a	Phenyl	48–51 (0.7)[a]		49.5
1b	Phenyl	124–126 (0.6)[b]		35.3
2a	*o*-Chlorophenyl	70–71 (0.7)[c]		30.0
2b	*o*-Chlorophenyl	148–153 (0.3)[b]	92–94	16.4
3a	*p*-Chlorophenyl	67–69 (0.3)[d]		20.2
3b	*p*-Chlorophenyl	143–146 (0.3)[e]	52–53	16.0
4a	*o*-Methylphenyl	67–68 (0.4)[f]		27.1
4b	*o*-Methylphenyl	146–147 (1.1)[h]		13.6
5a	*m*-Methylphenyl	58–60 (0.5)[i-l]		16.5
5b	*m*-Methylphenyl	135–138 (0.9)		16.1
6a	*p*-Methylphenyl	70–71 (0.7)		16.3
6b	*p*-Methylphenyl	129–130 (0.6)		16.1
7a	3-Chloro-4-methylphenyl	84–89 (0.8)[g]		19.3
7b	3-Chloro-4-methylphenyl	176–182 (1.1)		21.5
8a	2,4-Dichlorophenyl	88–91 (0.2)		17.6
8b	2,4-Dichlorophenyl	176–179 (0.3)		15.2
9a	1-Naphthyl	130–131 (0.8)[m, n]	51–54	9.7
9b	1-Naphthyl	227–229 (0.6)[o]	130–132	40.2

[a] E. L. Gefter, *Zh. Obshch. Khim.*, **28**, 1338 (1958) [*Chem. Abstr.*, **52**, 19999 (1958)] reports a boiling point of 58–59°C (0.8–1 mm) and B. Buchner and L. Lockhart, *J. Am. Chem. Soc.*, **73**, 755 (1951), give bp 95°C (15 mm). [b] M. P. Brown and H. B. Silver, *Chem. Ind. (London)*, 24 (1961), give bp 110–112°C (0.35 mm). [c] L. D. Quin and J. S. Humphrey, *J. Am. Chem. Soc.*, **83**, 4126 (1961), report bp 76–77°C (0.53 mm). [d] D. R. Nijk, *Recl. Trav. Chim. Pays-Bas*, **41**, 461 (1922), gives bp 132–133°C (20 mm). This substance was oxidized to *p*-chlorophenylphosphonyl dichloride, the NMR spectrum of which showed after phosphorus spin decoupling a A_2B_2 type of pattern which is consistent with the para substitution of the benzene ring. Further proof of this structure was obtained by hydrolysis of the *p*-chlorophenylphosphonyl dichloride to *p*-chlorophenylphosphonic acid, the melting point of which agreed with that reported (188°C) by G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951). [e] F. M. Kharrasova, G. Kh. Katai, R. B. Sultanova, and R. R. Shagidullin, *J. Gen. Chem. USSR (Engl. Transl.)*, **37**, 643 (1967), give mp 50–52°C. [f] B. Buchner and L. Lockhart, *J. Am. Chem. Soc.*, **73**, 755 (1951). [g] L. D. Quin and J. S. Humphrey, *J. Am. Chem. Soc.*, **83**, 4126 (1961), report bp 117–118°C (2.0 mm). [h] V. M. Plets, Dissertation, Kazan, 1938, reports mp 37°C and bp 253–257°C (15 mm). [i] P. Melchinger, *Ber.*, **31**, 2915 (1898). [j] A. Michaelis, *Justus Liebigs Ann. Chem.*, **293**, 193 (1896). [k] **294**, 1 (1896). [l] A Michaelis and H. Lange, *Ber.*, **8**, 1313 (1875). [m] M. Green and R. F. Hudson, *J. Chem. Soc.*, 3129 (1958), report mp 54°C and bp 118–120°C (0.5 mm). [n] T. Weil, B. Prjs, and H. Erlenmeyer, *Helv. Chim. Acta*, **36**, 1314 (1953), give mp 55°C and bp 135–137°C (0.5 mm). [o] A. B. Burg and R. I. Wagner, U.S. Patent 2,934,564, report bp 270–280°C (15 mm). [p] All compounds listed in Table II had C, H, P, and Cl analyses within 0.4% of theoretical.

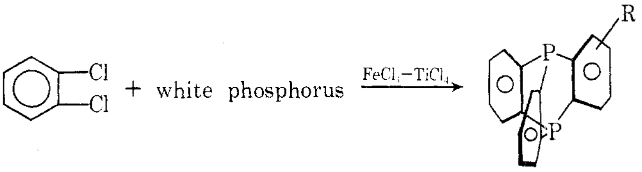
Table II
Reaction of 540 g of *o*-Dichlorobenzene with 70 g of White Phosphorus

Expt	Lewis acid catalyst	Temp, °C	Reaction time, hr	Products
A	8 g $FeCl_3$	325	7	76 g **2a** 80 g **2b** no **10**
B	1.3 g $TiCl_4$	300	7	141 g **2a** 134 g **2b** 1 g **10**
C	1.3 g $TiCl_4$ + 7 g $FeCl_3$	325	4	116 g **2a** 64 g **2b** 45 g **10**

di(*o*-chlorophenyl)phosphinous chloride, some phosphorus trichloride, and unreacted *o*-dichlorobenzene.

The crystalline substance was separated from the liquid by filtration and recrystallized from tetrachloroethylene. The purified material melted at 313–315°C (corrected). Gas chromatographic analysis revealed that in addition to the main product an impurity (about 6%) was present which was removed by further recrystallization from tetrachloroethylene.

The results of the elemental analyses suggested that the new compound had the empirical formula $C_{18}H_{12}P_2$. This was confirmed by the mass spectrum of **10**, which showed a strong parent peak at *m/e* 290. On the basis of these data structure **10** was proposed for this substance. **10** is a novel bicyclic 5,10-*o*-benzeno-5,10-dihydrophosphanthrene which we named 1,6-diphosphatriptycene.



10, R = H
11, R = Cl

In agreement with the structure proposed for **10**, its NMR spectrum showed two groups of aromatic protons, one in the area from 481 to 470 Hz and the other one in the area from 437 to 427 Hz. Furthermore, the areas under the peaks indicated that both groups of protons are present in equal numbers. The one group belongs to the protons in ortho position to each of the P atoms, the other group to the corresponding protons in meta position to the P atoms. The splitting in this spectrum is very complex, since the molecule has 14 nuclei with spins of ½ (12 ^1H and 2 ^{31}P). The coupling of protons in different rings to the ^{31}P nuclei makes them interdependent. This interdependence, however, may be removed by spin decoupling the ^{31}P. Assuming that structure **10** is correct and that protons in different rings are not coupled, the expected spectrum then should show independent sets of only four spins grouped into two symmetrically equivalent pairs. The spectrum obtained in this spin-decoupling experiment was exactly identical with that expected for structure **10** and provided final proof for the correctness of this structure.[7]

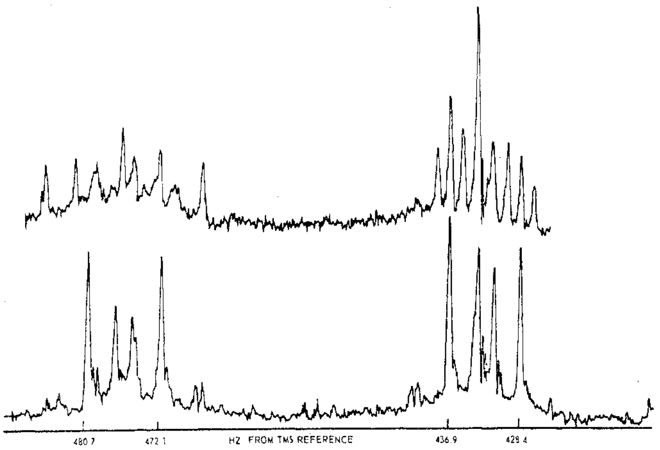
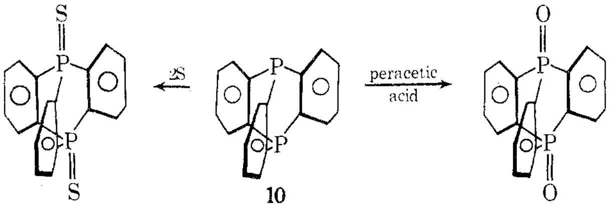


Figure 1. Top: NMR spectrum of diphosphatriptycene (ν_0 (Me_4Si) = 5994716 Hz). Bottom: ^1H spectrum with ^{31}P decoupled (ν_1 = 24285265 Hz).

The impurity accompanying the 1,6-diphosphatriptycene before recrystallization from tetrachloroethylene is according to its mass spectrum a monochloro 1,6-diphosphatriptycene (parent peak in mass spectrum *m/e* 324) which has structure **11**.

Oxidation of 1,6-diphosphatriptycene (**10**) with peracetic acid produced 1-6-diphosphatriptycene dioxide (**12**), while treatment of **10** in warm carbon disulfide with sulfur gave 1,6-diphosphatriptycene disulfide (**13**).



13 10 12

Effect of Catalyst on Formation of 1,6-Diphosphatriptycene. In a preliminary communication[8] we had reported the synthesis of 1,6-diphosphatriptycene (**10**) at 281°C using ferric chloride alone as catalyst. Since then, we have experienced very little success in repeating this synthesis. We believe, therefore, that the initial success in preparing **10** with ferric chloride alone at 281°C has been due to some unusual activity of the ferric chloride used in those early experiments (possibly because it contained traces of titanium tetrachloride).

Experimental Section

The elemental phosphorus (N.F. yellow sticks) used was purchased from Fisher Scientific Co., Fair Lawn, N.J. The melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ir spectra were recorded on a Beckman IR 4 infrared spectrophotometer. Mass spectra were taken on an AEI MS-12. The microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Clark Microanalytical Laboratory, Urbana, Ill.

General Remarks. All reactions were carried out in a Pyrex glass tube of 20 in. length, 2.25 in. o.d., and 3/16 in. wall thickness. The charging of the tube with the catalyst, phosphorus, and the aryl halide was done under argon or nitrogen. Before sealing the tube it was cooled in dry ice–acetone. After sealing the tube was wrapped with asbestos paper and inserted into a 3-l. rocking autoclave. About 360 ml of hexane was added to the autoclave as a heat exchange medium and to provide an outside pressure on the glass. Then the autoclave was pressurized with 500 psi of nitrogen and heated to the reaction temperature.

After the reaction was completed the tube was cooled in liquid nitrogen and opened.

Phenylphosphonous Dichloride (1a) and Diphenylphosphinous Chloride (1b). A mixture of 62 g (2 g-atoms) of elemental white phosphorus, 450 g (4 mol) of chlorobenzene, and 7.5 g (0.053 mol) of anhydrous aluminum chloride was heated for 8 hr at 350°C (see general remarks) in a sealed tube. After cooling, the reaction product was distilled in vacuo, yielding 180 g of phenylphosphonous dichloride (**1a**), bp 48–51°C (0.7 mm) (49.6% of theory based on phosphorus), and 155 g of diphenylphosphinous chloride (**1b**), bp 124–126° (0.6 mm) (34.7% of theory based on phosphorus).

***o*-Chlorophenylphosphonous Dichloride (2a), Di(*o*-chloro-**

phenyl)phosphinous Chloride (2b), and 1,6-Diphosphatriptycene (10). A mixture of 68.2 g (2.2 g-atoms) of elemental phosphorus, 588 g (4 mol) of *o*-dichlorobenzene, 7 g (0.043 mol) of anhydrous ferric chloride, and 1.3 g (0.0068 mol) of titanium tetrachloride was heated for 4 hr at 325°C (see general remarks) in a sealed tube. After cooling the reaction product was filtered through a coarse fritted glass filter funnel. The crystalline 1,6-diphosphatriptycene (**10**, 45 g) was washed with methanol and recrystallized from tetrachloroethylene. It melted at 313–315°C; ir spectrum (KBr) bands at 3050, 1431, 1258, 1230, 1160, 1102, 1085, 1050, 940, 745 and 725 cm^{-1}.

The filtrate was distilled in vacuo, yielding 50 g of phosphorus trichloride, 116 g of *o*-chlorophenylphosphonous dichloride (**2a**), and 64 g of di(*o*-chlorophenyl)phosphinous chloride (**2b**).

1,6-Diphosphatriptycene Dioxide (12). In a three-neck 500-ml flask, fitted with a stirrer, condenser, and dropping funnel, a clear, hot solution of 12 g of 1,6-diphosphatriptycene (**10**) in 250 ml of tetrachloroethylene was placed. Then 28 ml of a 25% peracetic acid solution in ethyl acetate was added slowly at about 90°C. The reaction was exothermic and the temperature rose to about 120°C while a white, crystalline precipitate separated. Stirring was continued with gentle heating for another 1 hr. After cooling to room temperature the crystalline material was filtered off and recrystallized from 1-propanol: mp 488–490°C; ir spectrum (in chloroform) bands at 3020, 2375, 1450 m, 1240, and 1120 cm^{-1}.

Anal. Calcd for $C_{18}H_{12}P_2O_2$: C, 67.08; H, 3.72; P, 19.25. Found: C, 67.35; H, 3.73; P, 19.18.

1,6-Diphosphatriptycene Disulfide (13). To a solution of 2.9 g of 1,6-diphosphatriptycene in 70 ml of carbon disulfide was added a slurry of 0.64 g of sulfur in 50 ml of carbon disulfide. The mixture was refluxed for 4 hr. After standing overnight at room temperature the reaction mixture was filtered and the filtrate evaporated to dryness at reduced pressure. The crude material (4.2 g) melts at 400–402°C and was recrystallized from 300 ml of hot ethyl acetate: melting point of recrystallized product 396–399°C; ir spectrum (in chloroform) bands at 3010, 2375, 1450, 1268, 1235, 1110, and 1055 cm^{-1}.

Anal. Calcd for $C_{18}H_{12}P_2S_2$: C, 61.02; H, 3.38; P, 17.51; S, 18.07. Found: C, 61.30; H, 3.45; P, 17.30; S, 17.79.

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Registry No.—**1a**, 644-97-3; **1b**, 1079-66-9; **2a**, 1004-78-0; **2b**, 32186-89-3; **5b**, 13685-23-9; **6a**, 1005-32-9; **6b**, 1019-71-2; **7b**, 36024-98-5; **8a**, 56783-19-8; **8b**, 56783-20-1; **10**, 31634-70-5; **12**, 31634-72-7; **13**, 56783-21-2; phosphorus, 7723-14-0; chlorobenzene, 108-90-7; *o*-dichlorobenzene, 95-50-1.

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(8) For a more detailed discussion of the NMR spectrum of 1-6-diphosphatriptycene see K. G. Weinberg and E. B. Whipple, *J. Am. Chem. Soc.*, **93**, 1802 (1971); see also K. G. Weinberg, U.S. Patent 3,651,147 (1972) (assigned to Union Carbide Corp.).

Comparative Stereochemistry of Catalytic and Diimide Reductions of Alkenes[1ab]

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The stereochemistry of the reduction of alkenes by diimide is compared with the stereochemistry of catalytic hydrogenation. Within selected groups of alkenes, mainly alkylidenecycloalkanes, the relation between the structure of the alkene and the ratio of saturated stereoisomers formed with diimide parallels that obtained on a platinum catalyst at high hydrogen pressures. This kind of correlation is not general; however, the comparisons afford a qualitative estimate of the importance and manner in which intramolecular, nonbonded interactions affect the stereochemistry of these reductions and help reveal the occurrence of exceptional catalytic mechanisms. The cis and trans 1-alkyl-4-*tert*-butylcyclohexanes which were obtained are separable by GLC (300 ft capillary coated with Apiezon L); the more stable trans isomer precedes the cis if the 1-alkyl group is methyl or ethyl but the elution order is reversed if the substituent is 2-propyl or *tert*-butyl.

The mechanism for the transfer of hydrogen from diimide (diimine or diazene)[2] to a carbon–carbon double bond is believed to consist of a single elementary process, the two hydrogen atoms being transferred simultaneously from nitrogen to carbon.[3] The apparent simplicity of the reaction commends it as a reference for the study of the stereochemistry of other cis addition reactions, and indeed van Tamelen and Timmons have compared the proportions of geometrical isomers obtained on the reduction of several olefins by diimide with the proportions obtained from catalytic hydrogenation, but the treatment was cursory.[4] In this paper we extend this comparison to learn how it may assist the disentanglement of the complex mechanisms of catalytic hydrogenation.

Substituted cyclo- or semicyclic alkenes, which yield a pair of geometrical isomers via cis addition to the opposite faces of the double bond, are suitable objects of this study. The ratio of isomers (cis/trans), which is obtained from a particular alkene upon reduction with diimide, is a measure of the difference in conformational energy of the diastereomeric transition states of the product controlling reaction, one leading to the cis isomer, the other to the trans. Because diimide is a small molecule, nonbonding interactions between it and the alkene at the transition state are likely to be small and virtually the same for both approaches.[3] Apparently, there are a few exceptions to this expectation.[4,5]

If other reducing agents are used, the ratio may be different because in comparison to the transition state for reduction by diimide, (1) the reaction centers have a completely