is in effect about 50 times that of any position in benzene.

A part of the reactivity of [2.2]paracyclophane may be attributed to the presence of the four methylene groups. *p*-Xylene was selected as a model compound for estimating the magnitude of this effect[10] and the reactivity of this arene, relative to benzene, was measured under the same reaction conditions employed for the phenylation of [2.2]paracyclophane. The total rate factor of *p*-xylene was found to be 2.4, in good agreement with the value of 2.7 reported by Huisgen and Sorge[11] before the advent of glpc. Therefore, the total and partial rate factors for homolytic phenylation of [2.2]paracyclophane, relative to *p*-xylene, are 14 and 7, respectively. If the argument advanced in the preceding paragraph is accepted, the sterically corrected reactivity at each position in [2.2]paracyclophane is 14 times as great as that of any site in *p*-xylene. Such rate enhancement could arise from transannular stabilization of and/or relief of strain in the transition state leading to the intermediate or cyclohexadienyl type of radical. An examination of molecular models of this radical reveals that strain may be relieved if the radical adopts a nonplanar conformation. However, any effect of this kind must be largely counterbalanced by a loss in delocalization energy in the ring undergoing substitution. The alternative interpretation is transannular delocalization through σ–π overlap in the planar radical. Since substantial amounts of this type of bonding could be maintained in a nonplanar radical, it is not inconceivable that both effects, relief of strain and transannular delocalization, contribute to rate enhancement in homolytic, and possibly electrophilic, aromatic substitution of [2.2]paracyclophane.[12]

Experimental Section[13]

4-Phenyl[2.2]paracyclophane.—Solid N-nitrosoacetanilide (12 g) was added to a solution of 1.08 g of [2.2]paracyclophane in 50 ml of pyridine at 65° under nitrogen and with stirring. After reaction, the pyridine was removed under vacuum and the residue was dissolved in 50 ml of methylene chloride. This solution was extracted with dilute hydrochloric acid, washed with water, dried, concentrated, and placed on an alumina column (Woelm, neutral, activity grade 1). Elution with cyclohexane gave an oil which was crystallized from methanol–cyclohexane–absolute ethanol. Recrystallization from absolute ethanol gave 76 mg of 4-phenyl[2.2]paracyclopame: mp 114–116°; $\lambda_{\max}^{\mathrm{EtOH}}$ 222 mμ (log ϵ 4.47); nmr (CCl_4, internal TMS) τ 2.57 (five aromatic protons), 3.48 (seven aromatic protons), and a complex multiplet centered at 6.9 (eight methylene protons).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.87; H, 7.05.

Treatment of 4-amino[2.2]paracyclopane[3] with isoamyl nitrite in benzene[4] gave impure material in low yield. However, the major component of this mixture exhibited the same retention time (glpc) as the sample prepared as described above.

Phenylation of [2.2]Paracyclophane.—N-nitrosoacetanilide (100 mg), 25 mg (0.120 mmole) of [2.2]paracyclophane, and 1.00 ml (11.2 mmoles) of benzene were dissolved in 5 ml of pyridine in a 6-in., side-arm test tube under nitrogen. After standing at 25–30° overnight, the mixture was dissolved in 35 ml of methylene chloride. This solution was extracted with two portions of dilute hydrochloric acid, washed with water, and dried, and the solvent was removed under reduced pressure. The residue was dissolved in the minimum amount of benzene, and *p*-chlorobiphenyl and pyrene were added as internal standards. Analyses were accomplished with a pair of 6 ft × $^1/_8$ in. columns packed with 10% SE-30 on 80–100 mesh Chromosorb P. Total rate factors and recoveries were measured by programming from 125 to 250° at 4 and 8°/min, respectively. The results are given in Table I.

Phenylation of *p*-Xylene.—To a 6-in., side-arm test tube were added 150 μl (1.21 mmoles) of *p*-xylene, 1.00 ml (11.2 mmoles) of benzene, 5 ml of pyridine, and 100 mg of N-nitrosoacetanilide under nitrogen. After reaction, the products were isolated and analyzed as described above for the phenylation of [2.2]paracyclophane except that naphthalene was used as the internal standard. Authentic 2,5-dimethylbiphenyl was prepared from 2,5-dimethylaniline by treatment of this amine with isoamyl nitrite in benzene.[4] Duplicate runs gave a total rate factor of 2.42 ± 0.04 (lit.[11] 2.7). None of the products of this reaction exhibited a retention time corresponding to that of authentic 4,4′-dimethylbibenzyl.

Registry No.—[2.2]Paracyclophane, 1633-22-3; 4-phenyl[2.2]paracyclophane, 7603-30-7; biphenyl, 92-52-4.

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[10] No model is entirely satisfactory. For example, 1,4-diethylbenzene was considered and rejected because previous studies of the phenylation of ethylbenzene have revealed some steric hindrance to reaction at the *ortho* positions in this arene: G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960, p 76.

[11] R. Huisgen and G. Sorge, *Ann.*, **566**, 162 (1950).

[12] See ref 2 for an assessment of strain in the cation and the conclusion that formation of this species may lead to an increase in strain.

[13] Melting points are corrected. Ultraviolet and nmr spectra were observed on Cary Model 14 and Varian A-60 spectrophotometers, respectively. An F & M Model 810 gas chromatograph with dual hydrogen-flame detectors and a Disc integrator were employed to determine the reactivity data. Elemental analyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of Diphenylphosphinyl Azide with Diphenylphosphine

Reinhold H. Kratzer and Kay L. Paciorek[1a]

MHD Research, Inc., Newport Beach,
California 92663

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The phosphonitrilic derivatives of the general formula $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_nOH$, where $n = 1$ and 3, are easily accessible by the hydrolysis of $[(C_6H_5)_2P(NH_2)NP(C_6H_5)_2(NH_2)]Cl$[1b] and $(C_6H_5)_2P(O)[N{=}P\,C_6H_5)_2]_3Cl$[2], respectively. The compound with $n = 2$ to date was obtained only as a reaction by-product in very poor yield.[2] The peculiar interaction of triphenylsilyl azide with diphenylphosphine[3] should be adaptable to the preparation of $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_2OH$, providing the rearrangement step of this reaction is a general one and independent of the type of azido compound subjected to reaction with a secondary phosphine.

Thus equimolar amounts of diphenylphosphinyl azide and diphenylphosphine were mixed in benzene solution at room temperature. Nitrogen evolution was observed after an incubation period of about 5 min, whereas the reaction between triphenylsilyl azide and diphenylphosphine required heating to 138°.[3] The desired product (II) was obtained in a 64% yield [based on $(C_6H_5)_2P(O)N_3$ employed], together with a small quantity of what is believed to be the intermediate I of the following reaction sequence. In

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[1] (a) The Marquardt Corp., Newport Beach, Calif. 92663; (b) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

[2] K. L. Paciorek, *ibid.*, **3**, 96 (1964).

[3] K. L. Paciorek and R. H. Kratzer, *J. Org. Chem.*, **31**, 2426 (1966).

$$(C_6H_5)_2P(O)N_3 + (C_6H_5)_2PH \longrightarrow \underset{\text{I}}{(C_6H_5)_2P(O)NHP(C_6H_5)_2} + N_2$$

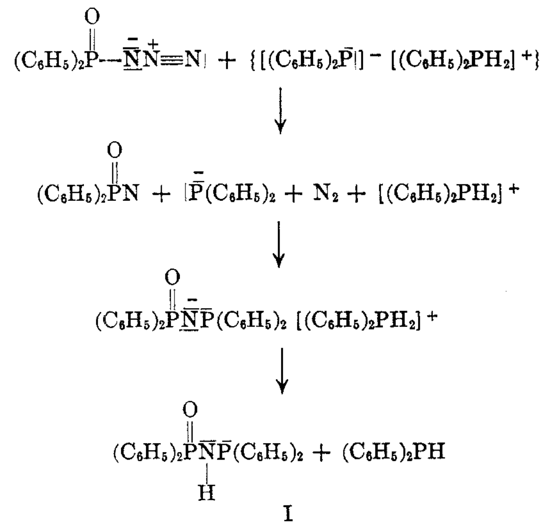
$$(C_6H_5)_2P(O)N_3 + (C_6H_5)_2P(O)NHP(C_6H_5)_2 \longrightarrow N_2 + \underset{\text{II}}{(C_6H_5)_2P(O)NHP(C_6H_5)_2{=}NP(O)(C_6H_5)_2}$$

contrast to the behavior of triphenylsilyl azide toward diphenylphosphine, the interaction of a 2:1 ratio of $(C_6H_5)_2P(O)N_3$ and $(C_6H_5)_2PH$ in benzene at room temperature failed to give identifiable products, although no starting materials appeared to be present after a 5-hr period. Mixing of the same ratio of the starting compounds in the absence of solvent resulted in a violent reaction from which, after heating at 110° for 20 hr, only the cyclic diphenylphosphonitrilic trimer and tetramer could be isolated in 30 and 5% yields, respectively [based on $(C_6H_5)_2P(O)N_3$ employed]. Exposure of the remaining product mixture to the atmosphere afforded diphenylphosphinic acid [10% yield, based on the sum of $(C_6H_5)_2PH$ and $(C_6H_5)_2P(O)N_3$ originally employed] which was probably derived from the unreacted starting materials.

The successful synthesis of $(C_6H_5)_2P(O)NHP(C_6H_5)_2{=}NP(O)(C_6H_5)_2$, which tautomerizes to $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_2OH$, shows that the hypothetical rearrangement $N{=}P(H)< \rightarrow NHP<$ is general for the oxidation of PH-containing materials by silyl azides,[3] aryl azide,[4] and phosphinyl azide. The fact that the 1:1 reaction yields only 32% of the desired product (based on diphenylphosphine), and the 1:2 reaction yields none of this product, tends to confirm earlier findings[3] that diphenylphosphine is involved in the production of $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_2OH$ to a greater extent than expressed by the above equation. It is conceivable that an excess of diphenylphosphine is necessary to act as a proton transfer agent, *e.g.*, in the form of a phosphonium ion, $(C_6H_5)_2PH_2^+$. Such a mechanism would avoid the necessity of postulating "self-reduction" of a pentavalent phosphorus involved in a bond to hydrogen. Phosphonium salts are known

$$(C_6H_5)_2P(O)N{=}\overset{+5}{P}(C_6H_5)_2H \longrightarrow (C_6H_5)_2P(O)NH\overset{+3}{P}(C_6H_5)_2$$

to decompose under the influence of base to form the corresponding phosphine. One of the possible intermediates of the following reaction sequence can be expected to be strongly basic.



$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}{-}\bar{\underline{N}}\overset{+}{N}{\equiv}N| + \{[(C_6H_5)_2\bar{P}|]^- [(C_6H_5)_2PH_2]^+\}$$

$$\downarrow$$

$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}N + |\bar{P}(C_6H_5)_2 + N_2 + [(C_6H_5)_2PH_2]^+$$

$$\downarrow$$

$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}\bar{\underline{N}}P(C_6H_5)_2\ [(C_6H_5)_2PH_2]^+$$

$$\downarrow$$

$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}\underline{N}\underset{H}{\underset{|}{\bar{P}}}(C_6H_5)_2 + (C_6H_5)_2PH$$

I

From the experimental data it is obvious that this reaction intermediate (I) is preferentially oxidized by diphenylphosphinyl azide to yield $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_2OH$, since only a very small amount of $(C_6H_5)_2P(O)NHP(C_6H_5)_2$ was isolated.

Experimental Section

The reactions were conducted either in a vacuum system or in a nitrogen atmosphere with rigid exclusion of moisture and oxygen. All chemicals were purified by applicable methods. Diphenylphosphine, bp 163–163.5° (14.8 mm), was obtained by the method of Kuchen and Buchwald[5] in 51% yield; diphenylphosphinyl azide was prepared in quantitative yield by interaction of diphenylphosphinyl chloride and trimethylsilyl azide.[6] Melting points were determined in sealed capillaries and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer double-beam (Model 21) infrared spectrophotometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_2OH$.—At room temperature to a vigorously stirred solution of $(C_6H_5)_2P(O)N_3$ (2.98 g, 0.012 mole) in benzene (25 ml) was added $(C_6H_5)_2PH$ (2.32 g, 0.012 mole) in benzene (25 ml). The addition took approximately 5 min; only after an additional 5-min interval was gas evolution observed. The solution discolored to deep yellow. Stirring at room temperature was continued for 18 hr; after this time only a yellow tinge remained. The infrared spectrum of the benzene solution did not exhibit any absorption in the vicinity of 2100 cm^{-1} which pointed to the absence of azido groups. Benzene was removed *in vacuo* when partial crystallization of the residue took place. The desired product was extracted from the residue with hot heptane. Evaporation of heptane afforded 2.34 g (64% yield, based on diphenylphosphinyl azide) of crystals, mp 148–149°. Subsequent crystallization from ethanol, followed by drying *in vacuo* at 100° for 24 hr gave pure $(C_6H_5)_2P(O)NP(C_6H_5)_2NHP(O)(C_6H_5)_2$ mp 150–151°.

Anal. Calcd for $C_{36}H_{31}N_2O_2P_3$: C, 70.12; H, 5.07; N, 4.54; P, 15.10; mol wt, 616. Found: C, 70.10; H, 5.09; N, 4.38; P, 15.20; mol wt, 600 (concentration, 0.047 *M*, in benzene using a Mechrolab osmometer). The material was found to be identical with that obtained previously[2] by the comparison of the infrared spectra and mixture melting point.

The hot heptane-insoluble portion was crystallized from a benzene–heptane mixture, mp 171–173° (0.07 g). This material exhibited (in Nujol mull) the following bands in the infrared region 1440 to 650 cm^{-1}: 1435 m (PC_6H_5), 1380 s (Nujol), 1350 w, 1333 w, 1180 s (P=O), 1123 m (tetracovalent phenyl-substituted phosphorus), 1108 m (trivalent phenyl-substituted phosphorus), 1070 w, 1027 w, 998 w, 942 s (PNH), 800 m, 743 s, 724 s, 692 s. From these infrared data and from the elemental analysis, as well as molecular weight determination, the heptane-insoluble material can be assumed to be $(C_6H_5)_2P(O)NHP(C_6H_5)_2$.

Anal. Calcd for $C_{24}H_{21}NOP_2$: C, 71.82; H, 5.27; N, 3.49; P, 15.43; mol wt, 401.39. Found: C, 72.90; H, 5.32; N, 3.85; P, 15.36; mol wt, 420 (concentration, 0.046 *M*, in benzene using a Mechrolab osmometer).

Registry No.—Diphenylphosphinyl azide, 4129-17-3; diphenylphosphine, 829-85-6; II, 759-47-0; I, 7648-76-2.

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