The anils of *o*-azidoaniline, that are listed in Table I, were decomposed by heating in dimethylformamide. In each case, the azide was found to decompose at about 130°. With one exception, cyclization occurred to give the anticipated 2-substituted benzimidazole (VI). The yields obtained are listed in Table II.

TABLE II

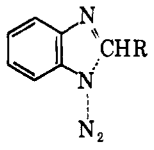
2-SUBSTITUTED BENZIMIDAZOLES

Benzimidazole	Yield, %	M.p., °C.
2-(*p*-Nitrophenyl)-	48[a]	318[b]
2-(*o*-Nitrophenyl)-	56[c]	208[d]
2-(*p*-Cyanophenyl)-	53[e]	262.5[f]
2-(*o*-Pyridyl)-	52[g]	215.5[h]
2-(*p*-Pyridyl)-	48[i]	216[j]
2-(*o*-Nitrostyryl)-	62[a]	216[k]
2-(2-Quinoxalinyl)-	71[a]	255[l]
2-Diphenylmethyl-	0	*m*

[a] Recrystallized from ethanol. [b] Lit.[7] m.p. 322°. No mixture melting point depression with authentic sample. [c] Recrystallized from methanol. [d] R. Walther and T. Pulawski [*J. prakt. Chem.*, **59,** 261 (1899)] report m.p. 208°. [e] Recrystallized from chloroform. [f] Lit.[8] m.p. 260°. Infrared spectrum was identical with that of an authentic sample. [g] Recrystallized from aqueous methanol. [h] B. L. Bastic [*Bull. soc. chim. Belgrade*, **16,** 141 (1951)] reports m.p. 217°. [i] Recrystallized from water. [j] R. Meyer and J. Maier [*Ann.*, **327,** 50 (1903)] report m.p. 214°. [k] H. Rupe and A. Porai-Koschitz [*Chem. Zentr.*, **75I,** 102 (1904)] report m.p. 215°. [l] *Anal.* Calcd. for $C_{15}H_{10}N_4$: C, 73.2; H, 4.06; N, 22.7. Found: C, 72.8; H, 4.27; N, 22.7. [m] No crystalline compound could be isolated.

The structures of two of the benzimidazoles were verified by independent synthesis. The procedure of Hinsberg and Funk[7] was used to prepare a sample of 2-(*p*-nitrophenyl)benzimidazole and the procedure of Stephen and Bower[8] was used to prepare a sample of 2-(*p*-cyanophenyl)benzimidazole. These compounds were found to be identical with the products produced by decomposing *p*-nitrobenzal *o*-azidoaniline and *p*-cyanobenzal *o*-azidoaniline, respectively.

The decomposition temperature (130°) of the anils of *o*-azidoaniline is 20–30° below that of phenyl azide. The lower decomposition temperature suggests that the reaction is concerted, involving considerable participation by carbon in the transition state (VII).



VII

Krbechek and Takimoto[3b] reported that the anils of *o*-azidoaniline, which they prepared, decompose at *ca.* 140°. Their compounds included benzal and *p*-methylbenzal *o*-azidoanilines. The results of their work and the work reported here suggest that the decomposition temperature is not very dependent on the nature of substituents and hence that the transition state is not particularly polar.

Experimental[9]

Preparation of Anils from *o*-Azidoaniline.—The anils were prepared by condensing *o*-azidoaniline[4] with an equimolar quantity of the corresponding aldehyde in benzene solution. The water formed was azeotroped out of the reaction by distilling the benzene. This was done under vacuum at temperatures below 35° to prevent decomposition of *o*-azidoaniline (decomposition temperature *ca.* 65°). The following procedure is typical.

o-Azidoaniline (1.0 g., 0.0074 mole) and *p*-nitrobenzaldehyde (1.1 g., 0.0074 mole) were dissolved in 100 ml. of anhydrous benzene. The reaction mixture was warmed to 35°, and the benzene was slowly distilled under vacuum. The crude residue was recrystallized from ethanol to give 1.01 g. (51%) of yellow *p*-nitrobenzal *o*-azidoaniline, m.p. 132°.

Preparation of 2-Substituted Benzimidazoles.—The anils of *o*-azidoaniline were all decomposed by heating them in dimethylformamide. The following procedure is representative. In 25 ml. of dimethylformamide was dissolved 1.0 g. of *o*-nitrocinnamal *o*-azidoaniline. The solution was refluxed for 2 hr. After cooling, the solution was poured into water to precipitate the crude product. The solid was filtered off and recrystallized from ethanol. The yield of 2-(*o*-nitrostyryl)benzimidazole was 0.45 g. (62%), m.p. 216°.

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[7] O. Hinsberg and F. Funk, *Ber.*, [3] **27,** 2191 (1894).

[8] F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 2971 (1949).

[9] Melting points are corrected. They were obtained using a Thomas-Hoover capillary melting point apparatus.

Bromine Addition to N-(Diarylphosphinyl)iminophosphoranes

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Diarylphosphinic azides have been found to react with a variety of tertiary phosphorus compounds to yield N-(diarylphosphinyl)iminophosphoranes.[1] As a result of continuing studies in this area, we now wish to report on the novel addition of bromine to the N-(diarylphosphinyl)iminophosphoranes.

During the attempted nuclear bromination of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (I) in carbon tetrachloride by means of bromine and iron powder, it was observed that there was not any evolution of hydrogen bromide with the concurrent precipitation of a yellow-orange crystalline material. These results then suggested that the bromine was reacting additively to yield a phosphorane dibromide II rather than substituting the aromatic groups of I. This novel bromination was, however, complicated somewhat by the inclusion of chlorine in the yellow-orange crystalline product when the addition was carried out in carbon tetrachloride and by apparently low bromine contents of the products from reactions in benzene or chloroform. The low bromine content was reflected in the high (~106%) yields of the phosphorane I recovered from the hydrolysis studies.

$$\underset{\text{I}}{(C_6H_5)_2P(O)N{=}P(C_6H_5)_3} + Br_2 \underset{\text{acetone–water}}{\rightleftarrows} \underset{\text{II}}{(C_6H_5)_2P(O)N{=}P(C_6H_5)_3Br_2}$$

Hydrolysis of the yellow-orange solids with dilute sodium hydroxide or simply with acetone and water resulted in the nearly quantitative recovery of the parent phosphorane I. In contrast, under the same mild conditions, nuclear halogen is not removed from the phenyl groups of the haloarylphosphorane III.

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[1] R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83,** 4466 (1961).

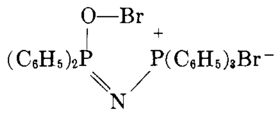
$$\underset{\text{III}}{(p\text{-ClC}_6\text{H}_4)_2\text{P(O)N}{=}\text{P(C}_6\text{H}_5)_3}$$

These results confirm the previous assumption of additive rather than substitutive bromination of I.

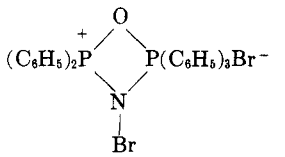
When II was briefly refluxed in acetone or methyl ethyl ketone in the absence of water, the yellow-orange color rapidly faded and the presence of a lachrymator was noted. In the experiment involving acetone, the presence of α-bromoacetone was confirmed by vapor phase chromatographic comparison with α-bromoacetone prepared according to the facile cupric bromide method of King and Ostrum.[2] Removal of the solvent and bromo ketone resulted in the recovery of the phosphorane hydrobromide IV. The identity of the phosphorane hydrobromide IV was further substantiated by the addition of gaseous hydrogen bromide to the phosphorane I. The hydrolysis of the phosphorane hydrobromide IV was equally facile and resulted also in the quantitative recovery of I.

$$\underset{\text{I}}{(\text{C}_6\text{H}_5)_2\text{P(O)N}{=}\text{P(C}_6\text{H}_5)_3} \xrightleftharpoons[\text{acetone--water}]{\text{HBr(g)}} \underset{\text{IV}}{(\text{C}_6\text{H}_5)_2\text{P(O)N}{=}\text{P(C}_6\text{H}_5)_3\text{HBr}}$$

While no definite assignments of structure for the dibromide can be made, the method of preparation, the analytical data and reactions suggest V and VI as possible structures. Since the yellow-orange phosphorane dibromide II reacted with acetone and methyl ethyl ketone to yield bromo ketones, the presence of a positive bromine in II is indicated. Infrared examination of II indicated a loss of the characteristic P–O absorption present in the parent phosphorane I at 1190 cm.$^{-1}$. While it is not possible to rule out a P–O shift completely to account for its disappearance, the similarity in the unchanged portions of the spectra make this appear unlikely to be the case. Since the P=N absorption at 1299 cm.$^{-1}$ was still present with the remainder of the spectrum being essentially unchanged, these combined results support only structure V for the dibromide II. Similarly, the phosphorane hydrobromide IV also shows the loss of the P–O absorption and the continued presence of a P=N absorption. New, broad, and shallow absorptions in IV at 2560–2100 and a sharp, strong absorption at 966 cm.$^{-1}$ are also found in the spectra of several diarylphosphinic acids. These data suggest a P–OH in IV in analogy to structure V advanced for II. Additionally, in support of this assignment for IV is the lack of any evidence for N–H absorptions in the potassium bromide pellet or Nujol mull of IV.



V



VI

Similar yellow-orange, labile bromination products have been obtained from N-(diphenylthiophosphinyl)-P,P,P-triphenyliminophosphorane, N-[(bis-p-tolyl)-phosphinyl]-P,P,P-triphenyliminophosphorane, N-[bis-(p-chlorophenyl)phosphinyl]-P,P,P-triphenyliminophosphorane, and N-(diphenylphosphinyl)-P,P,P-tris-(p-chlorophenyl)iminophosphorane.

Experimental

The infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. The vapor phase chromatographic study was done on a Perkin-Elmer 801 gas chromatograph equipped with a Model 194 integrator. The melting points are not corrected.

N-(Diphenylphosphinyl)-P,P,P-triphenyliminophosphorane Dibromide (II). A. With Iron Catalyst.—In a preliminary experiment, 0.2 g. of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane[1] (I) was partially dissolved in hot carbon tetrachloride containing iron powder before bromine in chloroform was added dropwise. After each drop there was loss of the red color and precipitation of an orange solid. The solids were filtered, dissolved in chloroform, and filtered to remove the iron powder. Concentration of the chloroform gave yellow-orange crystals which softened at 205° and melted at 220–225°. The infrared spectrum indicated P=N at 1299–1290, P—phenyl at 1117, and a loss of the P—O absorption at 1190 cm.$^{-1}$

B. In Carbon Tetrachloride.—To 4.8 g. (0.01 mole) of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (I) partially dissolved in 96.4 g. of hot carbon tetrachloride was added 3.3 g. of carbon tetrachloride containing 1.59 g. (0.01 mole) of bromine. The mixture was warmed for 15 min. on the steam bath and filtered, and the yellow solid was washed with 10 ml. of carbon tetrachloride to obtain 5.5 g. of yellow-orange crystals (0.00863 mole, 86.3% yield), m.p. 225–229°. The analytical sample was washed with warm benzene, carbon disulfide, and ethanol.

Anal. Calcd. for $\text{C}_{30}\text{H}_{25}\text{Br}_2\text{NOP}_2$: Br, 25.08; P, 9.72. Found: Br, 19.23; Cl, 2.66; P, 9.95.

C. In Benzene.—Addition of 16 g. (0.1 mole) of bromine in 44.2 g. of benzene to 47.8 g. (0.1 mole) of I dissolved in 600 g. of hot benzene resulted in the recovery of 58.7 g. (0.0922 mole, 92.2% yield) of orange solids, m.p. 220–230° (attempted recrystallization from chlorobenzene did not improve the melting point). The infrared spectrum of this material was, however, identical with those of the other preparations. V.p.c. examination of the recovered benzene showed the absence of any bromobenzene.

D. In Chloroform.—In this experiment, the addition of 16 g. (0.1 mole) of bromine dissolved in 42.7 g. of chloroform to 47.8 g. (0.1 mole) of phosphorane I dissolved in 133 g. of chloroform resulted in the precipitation of the orange solid. After 30 min. in an ice–water bath, filtration yielded 51.6 g. of yellow-orange solid. An additional 7.6 g. was recovered from the solvent yielding a total of 59.2 g. (0.0929 mole, 92.9% yield) of the dibromide II. After a wash with ethanol the melting point was 226–228°. The dibromide was insoluble in tetrahydrofuran, p-dioxane, and carbon disulfide and partially soluble in hot benzene and chlorobenzene. The infrared spectrum was identical with that of the material recovered from the previous run with iron powder.

Anal. Calcd. for $\text{C}_{30}\text{H}_{25}\text{Br}_2\text{NOP}_2$: Br, 25.08; N, 2.20; P, 9.72. Found: Br, 22.3; Cl, not detected; N, 1.97; P, 9.20.

Hydrolysis of II.—A 1.2863-g. (2.01 mmoles) quantity of II was dissolved in 150 ml. of acetone and 25 ml. of water on a steam bath. After 10 min. the yellow color had disappeared. During the removal of the acetone by means of a stream of air, a strong lachrymator was noted and was thought to be α-bromoacetone (see below). After the acetone had been removed, 1.0173 g. (2.13 mmoles, 106%) of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (I), m.p. 168–170°, was filtered from the remaining water. The aqueous filtrate was found to contain 2.14 mmoles of bromide which is equivalent to the loss of one-half of the total bromine from II as α-bromoacetone.

When 0.1596 g. (0.250 mmole) of the yellow-orange dibromide was allowed to stand on a steam bath for 7 hr. and then for 5 days in dilute sodium hydroxide solution, 0.1260 g. (0.264 mmole, 105.6% yield) of the parent phosphorane I, m.p. 166–170°, was recovered.

In a third experiment, 7.8 g. (0.0122 mole) of the dibromide II was similarly treated except that the acetone and α-bromoacetone were removed at reduced pressure prior to addition of water and subsequently were recovered from a Dry Ice trap. Vapor phase chromatographic comparison of the by-product α-bromoacetone

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(2) L. C. King and G. K. Ostrum, *J. Org. Chem.*, **29**, 3459 (1964).

with α-bromoacetone prepared from cupric bromide and acetone[2] indicated that the two were identical. Approximately 6.2 g. (0.013 mole, 106% yield) of phosphorane I, m.p. 168–170°, was recovered after the residual phosphorane hydrobromide was stirred with water for 30 min.

Attempted Hydrolysis of N-[Bis(*p*-chlorophenyl)phosphinyl]-P,P,P-triphenyliminophosphorane.—Under similar hydrolysis conditions, 0.0324 g. of the chlorophenylphosphorane III, m.p. 205–206°, was dissolved in 3 ml. of acetone and refluxed 10 min. before 3 ml. of water was added. Removal of the solvents left 0.0322 g. of unchanged III, m.p. 204–206°.

N-(Diphenylphosphinyl)-P,P,P-triphenyliminophosphorane Hydrobromide (IV). A. From Methyl Ethyl Ketone.—When 0.4128 g. (0.649 mmole) of the dibromide was warmed with 2.5 g. of methyl ethyl ketone, there resulted a loss of the yellow-orange color. On removal of the solvent, 0.4018 g. of a tacky white residue softening about 182° and melting at 195–200° was recovered.

Anal. Calcd. for $C_{30}H_{26}BrNOP_2$: Br, 14.31; N, 2.51; P, 11.09. Found: Br, 14.7; P, 10.9.

B. From Hydrogen Bromide.—Gaseous hydrogen bromide was passed through a −70° bath and then into a benzene solution of 10.7 g. (0.0224 mole) of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (I) until an oil formed. After standing about 6 weeks, the oil slowly crystallized. The mass of crystals was broken up, filtered under argon, and vacuum dried to yield 12.2 g. (0.0219 mole, 97.5% yield) of product, phosphorane hydrobromide IV, which appeared to soften at about 202° and melted at 210–214° (mostly at 213–214°).

Anal. Found: Br, 14.0; N, 2.45; P, 11.1.

Hydrolysis of IV.—Hydrolysis of 2.1103 g. (3.77 mmoles) of the phosphorane hydrobromide IV in 25 ml. of refluxing acetone was accomplished in 10 min. after the addition of 5 ml. of water, the material all dissolving in this time. Removal of the acetone yielded 1.7248 g. (3.61 mmoles, 95.6% yield) of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (I), m.p. 170–171°. The aqueous wash of the phosphorane was found to contain 3.68 mequiv. of bromide.

Acknowledgment.—We wish to express our thanks to Mr. Karl Sterner for the elemental analyses, to Mrs. Nancy Naumann for the infrared spectra, and to Mr. Kent Smitheman for the vapor phase chromatography.

11α-Alkylated Steroids. V. Aryllithium Additions to an 11-Oxo Steroid

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The addition of methyllithium to the sterically hindered 11-oxo group of steroids has been shown to occur in several instances[1] to give 11α-methyl-11β-hydroxy steroids. In order to determine if 11α-aryl steroids could be prepared in a corresponding manner, 3,3,20,20-bis(ethylenedioxy)-5β-pregnan-11-one[2] was treated with phenyllithium in ether. No formation of 11α-phenyl-11β-hydroxy steroid was observed. The use of 2-pyridyllithium, in contrast, afforded 3,3,20,20-bis(ethylenedioxy)-11α-(2-pyridyl)-5β-pregnan-11β-ol in 26% yield.

Since phenyl and pyridyl are approximately isosteric, an attempt was made to determine the relationship of steric and electronic factors to the addition reaction of aryllithium to an 11-oxo steroid. 3,3,20,20-Bis(ethylenedioxy)-5β-pregnan-11-one was treated with 2-methoxyphenyllithium and with 4-methoxyphenyllithium. The latter experiment gave a quantitative material balance, with no evidence of greater than 1% aryllithium addition. On the other hand, it was possible to isolate a 6% yield of the 2-methoxyphenylated steroid from the former experiment.

One may speculate from these results that in the case of 2-pyridyllithium and 2-methoxyphenyllithium internal coordination with metal provides an "open edge" for addition, whereas in the case of phenyllithium and 4-methoxyphenyllithium, where internal coordination cannot take place, an additional solvent molecule coordinates with metal and thus increases the steric hindrance to the addition reaction.[3]

Further reduction of steric effects by the use of α-picolyllithium resulted in a 52% yield of 3,3,20,20-bis-(ethylenedioxy)-11α-(2-pyridylmethyl)-5β-pregnan-11β-ol from 3,3,20,20-bis(ethylenedioxy)-5β-pregnan-11-one. Each of the bisketal products was hydrolyzed with acid to the corresponding 3,20-diones, namely, 11β-hydroxy-11α-(2-pyridyl)-5β-pregnane-3,20-dione, 11β-hydroxy-11α-(2-methoxyphenyl)-5β-pregnane-3,20-dione, and 11β-hydroxy-11α-(2-pyridylmethyl)-5β-pregnane-3,20-dione.

Experimental[4]

3,3,20,20-Bis(ethylenedioxy)-11α-(2-pyridyl)-5β-pregnan-11β-ol.—2-Pyridyllithium was prepared by adding 40.5 g. (256 mmoles) of 2-bromopyridine dropwise with stirring to 200 ml. of 1.3 *M* butyllithium[5] in ether cooled to 40° in a nitrogen atmosphere. To the resultant brown solution was added rapidly a solution of 20.9 g. (50 mmoles) of 3,3,20,20-bis(ethylenedioxy)-5β-pregnan-11-one in 150 ml. of benzene and 250 ml. of ether. The mixture was allowed to stand at room temperature for 3 days, and was then washed four times with water and evaporated to dryness. Trituration of the resultant thick red-brown oil (containing some crystals) with cold methanol (250 ml.) gave 5.28 g. of white crystalline 3,3,20,20-bis(ethylenedioxy)-11α-(2-pyridyl)-5β-pregnan-11β-ol, m.p. 219–223°. The filtrate residue was crystallized from Skellysolve B to give an additional 0.538 g. of the same compound, m.p. 222–228°. [Additional product (0.90 g., m.p. 217–225°) could be obtained by Florisil chromatography of the mother liquor, from which 2.95 g. of starting material, m.p. 131–143°, was also recovered.] For analysis a sample was recrystallized from methanol to m.p. 223–234°, $[\alpha]^{20}\text{D}$ +75° (*c* 1, acetone), λ_{max}^{EtOH} 264 mμ (A_m 3620).

Anal. Calcd. for $C_{30}H_{43}NO_5$: C, 72.40; H, 8.71; N, 2.81. Found: C, 72.04; H, 8.56; N, 2.86.

11β-Hydroxy-11α-(2-pyridyl)-5β-pregnane-3,20-dione was prepared as described above for the bisketal except that the total crude product was treated with methanolic sulfuric acid to hydrolyze the ketal groups. Repeated chromatography of the resultant red-brown tar afforded, from 4.18 g. of 3,3,20,20-bis-(ethylenedioxy)-5β-pregnan-11-one, 0.82 g. of crude 11β-hydroxy-11α-(2-pyridyl)-5β-pregnane-3,20-dione, in several crops, the average melting point of which was *ca.* 220–230°. The crude dione was recrystallized for analysis from acetone to m.p. 232–234°, λ_{max}^{EtOH} 263 mμ (A_m 3875).

Anal. Calcd. for $C_{26}H_{35}NO_3$: C, 76.24; H, 8.61; N, 3.42. Found: C, 76.20; H, 8.68; N, 3.80.

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(1) H. J. Ringold, E. Batres, and J. A. Zderic, *Tetrahedron,* **2**, 164 (1958); G. S. Fonken and J. A. Hogg, *ibid.*, **2**, 365 (1958); G. S. Fonken, *J. Org. Chem.*, **23**, 1075 (1958); G. S. Fonken, J. A. Hogg, and A. V. McIntosh, *ibid.*, **24**, 1600 (1959); J. Elks, *J. Chem. Soc.*, 3333 (1960).

(2) E. P. Oliveto, T. Clayton, and E. B. Hershberg, *J. Am. Chem. Soc.*, **75**, 486 (1953).

(3) The author is indebted to one of the referees for an alternative speculation, namely, "that phenyllithium is unreactive because of association with itself in solution and that the substituted compounds are more strongly solvated because of polarization, hence less associated, and therefore more reactive."

(4) Melting points were determined with the Fischer-Johns apparatus and are not further corrected. Infrared spectra were all consistent with the formulated structures. All analyses were performed by the Department of Physical and Analytical Chemistry of The Upjohn Company.

(5) H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 285 (1954).