lization from ether–petroleum ether, was obtained in 95% yield as colorless needles, mp 169–170°.

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80; neut equiv, 296. Found: C, 77.1; H, 6.8; neut equiv, 292.

Treatment of the acid with an ethereal solution of diazomethane afforded, after crystallization from ether–petroleum ether, a 91% yield of the methyl ester as colorless prisms, mp 82–84°. Repeated recrystallizations gave material, mp 85–86°, $\lambda_{max}^{CHCl_3}$ 5.78 μ (ester C=O). The nmr spectrum[4b] showed maxima for five aromatic protons at 6.83–7.78 ppm, three protons as a singlet at 3.85 ppm ($ArOCH_3$), three protons as a singlet at 3.74 ppm ($COOCH_3$), four protons as a singlet at 2.85 ppm ($-CH_2-CH_2-$ at C-9 and C-10), and three protons as a singlet at 2.38 ppm ($ArCH_3$).

Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.6; H, 7.2.

Methyl β-(2-Methyl-7-methoxy-1-phenanthryl)propionate (II).—A 0.110-g sample of the aforementioned ester I (R = CH_3), mp 84–85°, was heated in a sublimation apparatus under nitrogen at 286–292° for 15 min with 0.1 g of 5% palladium on carbon (Davison Chemical Co.). After cooling, the mixture was diluted with benzene and filtered, and the catalyst was washed thoroughly with hot ethyl acetate. The combined filtrate and washings were concentrated under reduced pressure, and the residue was crystallized from ether–petroleum ether to give 0.032 g of colorless prisms, mp 134.5–135.5°. Chromatography of the oily residue obtained from the mother liquor on 5 g of silicic acid yielded, on elution with benzene, an additional 0.04 g, mp 133–135°. Recrystallization of the major fraction gave material: mp 135–136°; $\lambda_{max}^{CHCl_3}$ 5.76 μ (ester C=O); $\lambda_{max}^{95\%\ EtOH}$ 302 mμ (ε 10,200), 290 (14,600), 279 (19,700), 258 (72,200), 234 (21,000), and 224 (21,300). The nmr spectrum[4b] showed maxima for seven aromatic protons at 7.10–8.54 ppm, three protons as a singlet at 3.82 ppm ($ArOCH_3$), three protons as a singlet at 3.65 ppm ($COOCH_3$), and three protons as a singlet at 2.46 ppm ($ArCH_3$).

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 78.15; H, 6.8.

The Cycloethylene Ketal of *dl*-Equilenin Methyl Ether.—A solution of 3.1 g of *dl*-equilenin methyl ether,[7] mp 187–188°, 6 ml of ethylene glycol, and 0.01 g of *p*-toluenesulfonic acid monohydrate in 200 ml of benzene was stirred with heating at reflux (atmosphere of nitrogen) in a system containing a water separator filled with Drierite. After 7 hr the solution was cooled and added to 5% potassium hydroxide solution. The organic layer was washed thoroughly with water, followed by saturated brine, and then dried over anhydrous sodium sulfate. The oily residue obtained on removal of the solvent under reduced pressure was triturated with ether. The resulting solid was crystallized from methylene chloride–methanol to give 2.84 g of the ketal, mp 131–132°. Repeated recrystallizations from ether–petroleum ether afforded colorless needles, mp 130–132°.

Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.9; H, 7.3.

The Cycloethylene Ketal (V) of *dl*-14,15-Dehydroequilenin Methyl Ether.—A 0.160-g specimen of the aforementioned ketal of *dl*-equilenin methyl ether, mp 131–132°, was treated with 0.23 g of dichlorodicyanobenzoquinone in 25 ml of benzene for 10 min at 25°. The mixture was processed as described above for the preparation of I (R = CH_2CH_2OH). Trituration of the crude product with ether, followed by crystallization from ether–petroleum ether, gave 0.12 g of colorless rods, mp 122–123°. Recrystallization afforded material: mp 122–123°; $\lambda_{max}^{CHCl_3}$ 9.62, 9.72 (C—O), and 10.5 μ (ethylenedioxy); $\lambda_{max}^{95\%\ EtOH}$ 352 mμ (ε 1900), 336 (1930), 304 (24,400), 292 (25,800), 281 (18,700), 263 (67,600), 253 (67,700), and 245 (49,600). The nmr spectrum[4b] showed maxima for five aromatic protons at 7.02–7.95 ppm, one proton as a triplet at 5.98, 6.03, and 6.08 ppm (C-15 H split by protons at C-16), four protons as a singlet at 3.98 ppm (ethylenedioxy), three protons as a singlet at 3.85 ppm ($ArOCH_3$), and three protons as a singlet at 1.09 ppm (C-18 CH_3).

Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.1; H, 6.6.

γ-(7-Methoxy-9,10-dihydro-1-phenanthryl)butyric Acid (VIII, R = H).—A 0.073-g sample of the cycloethylene ketal of *dl*-9-iso-18-nor-D-homoestrone methyl ether,[3] mp 131–132°, was treated with 0.16 g of dichlorodicyanobenzoquinone in 25 ml of benzene for 5 hr at 25°. The mixture was processed as described above for the preparation of I (R = CH_2CH_2OH), and the crude product was chromatographed on 5 g of basic alumina. The fraction eluted with 50% ether in ethyl acetate amounted to 0.035 g of crude hydroxy ester VIII (R = CH_2CH_2OH). Attempts to crystallize this material failed; therefore, it was saponified with aqueous methanolic potassium hydroxide to give crude solid acid in quantitative yield. Repeated recrystallizations from ether–petroleum ether gave colorless prisms, mp 138.5–139°, $\lambda_{max}^{CHCl_3}$ 5.85 μ, λ_{max}^{MeOH} 280 mμ (ε 18,400).

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.75; H, 7.0.

Acknowledgment.—Acknowledgment is made to the U. S. Public Health Service and the National Science Foundation for support of this research. We also wish to thank Dr. George Rosenkranz of Syntex S. A. for a gift of extremely pure estrone methyl ether.

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[7] Prepared by the method of W. S. Johnson, J. W. Petersen, and C. D. Gutsche [*J. Am. Chem. Soc.*, **69**, 2942 (1947)] under the auspices of the Wisconsin Alumni Research Foundation whom we thank for a gift of material.

The Synthesis of (2,4-Dinitrophenyl)- and (2,4,6-Trinitrophenyl)methylenephosphoranes

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As part of a program directed toward the preparation of stable methylenephosphoranes, we were interested in synthesizing disubstituted methylenephosphoranes, $(C_6H_5)_3P{=}CR_1R_2$, in which one of the substituents was a phenyl ring containing one or more nitro groups. In particular, compounds were desired in which the nitro groups were *ortho* and *para* since this positioning would allow greater delocalization of the negative charge on the methylene carbon and would, consequently, lead to enhanced stabilization of the methylenephosphorane system.[1]

Our initial approach involved the arylation of monosubstituted methylenephosphoranes I with the appropriate mono- or polynitrohalobenzene. Although monosubstituted methylenephosphoranes have been alkylated with alkyl halides[2] and acylated with acid chlorides,[3] no reaction of this type has been reported with aryl halides.[4,5]

Reaction of Ia and Ib with picryl chloride occurred readily in refluxing benzene and resulted in good yields (52–57%) of the disubstituted methylenephosphoranes IIa and b. Compounds IIa and b proved to be quite stable, being recovered unchanged on prolonged treatment with hot methanolic potassium hydroxide.

Extension of this synthesis to 2,4-dinitro-1-chlorobenzene gave less satisfactory results. A diminished

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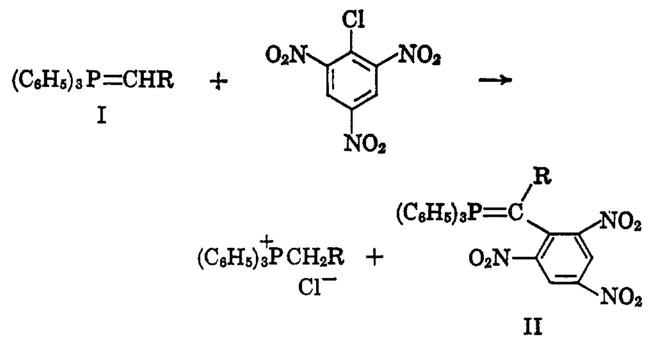
[1] F. Kröhnke, *Chem. Ber.*, **83**, 291 (1950).

[2] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); (b) H. J. Bestmann and H. Schulz, *Tetrahedron Letters*, **No. 4**, 5 (1960). (c) *Chem. Ber.*, **95**, 2921 (1962).

[3] (a) H. J. Bestmann, *Tetrahedron Letters*, **No. 4**, 7 (1960); (b) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961); (c) H. J. Bestmann and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962); (d) H. J. Bestmann and H. Schulz, *Ann.*, **674**, 11 (1964).

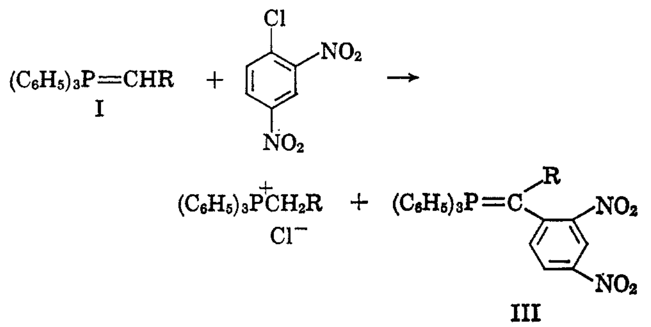
[4] A. Maercker, *Org. Reactions*, **14**, 291 (1965).

[5] E. Zbiral [*Tetrahedron Letters*, **No. 52**, 3963 (1964)] has reported the arylation of monosubstituted methylenephosphoranes with benzyne. Rearranged products were isolated with no apparent formation of the disubstituted methylenephosphoranes.



a, R = CO_2CH_3
b, R = CN

reactivity would be anticipated and, indeed, reaction with Ia and b was extremely sluggish in refluxing benzene, several days being required for completion. By operating in dimethylformamide at 100° the time of reaction could be reduced to 4 hr. In all cases, yields were in the 25–30% range.



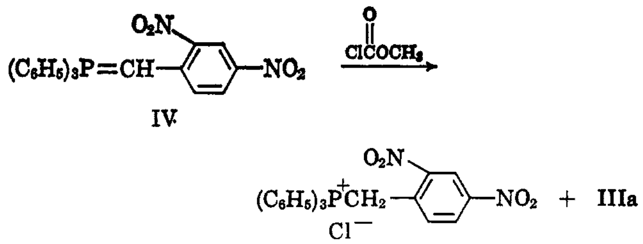
a, R = CO_2CH_3
b, R = CN

Phosphoranes IIIa and b exhibited the same inertness toward methanolic potassium hydroxide that was observed for IIa and b. In addition, they possessed thermochromic properties, turning darker when heated above 180° but returning to their original colors upon cooling.[6]

Attempted reaction of 4-nitro-1-bromobenzene with either Ia or b was unsuccessful. Prolonged heating in boiling xylene or dimethylformamide at 100° failed to give any phosphonium salt.

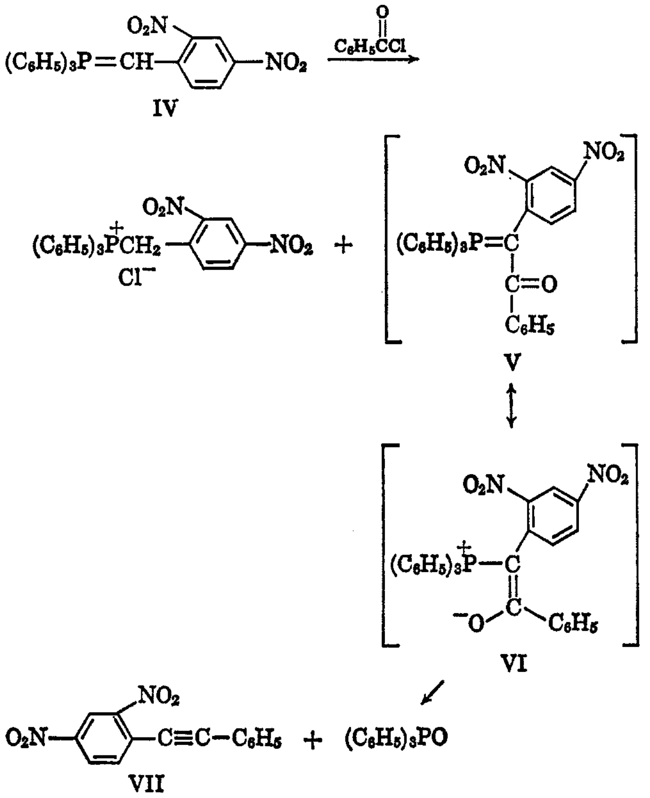
An alternate route to the synthesis of disubstituted methylenephosphoranes was also investigated, using 2,4-dinitrobenzylidenetriphenylphosphorane (IV) as starting material. Preparation of IV was carried out by treating triphenylphosphine with 2,4-dinitrobenzyl bromide followed by dehydrobromination of the phosphonium salt with aqueous base. Phosphorane IV was reasonably stable and could be kept at room temperature for a long period of time without any noticeable decomposition. However, in refluxing methanol it was readily cleaved to a mixture of 2,4-dinitrotoluene and triphenylphosphine oxide.

Acylation of IV with methyl chloroformate afforded a 23% yield of phosphorane IIIa which was identical in all respects with the product obtained above from the condensation of 2,4-dinitro-1-chlorobenzene with Ia. The recovery of a substantial amount of starting material IV after 40 hr reflux in benzene attests to the lack of reactivity between methyl chloroformate and IV.



Benzoylation of IV, on the other hand, occurred relatively faster and proceeded to completion after refluxing in benzene for 16 hr (see Scheme I). However, instead of the expected product, V, there was obtained an 83% yield of a 1:1 mixture of (2,4-dinitrophenyl)phenylacetylene (VII) and triphenylphosphine oxide. From this a 51% yield of pure acetylene VII was isolated. The decomposition of V to acetylene VII, presumably *via* intermediate VI, in refluxing benzene is of interest, for while analogous parallel transformations are known,[7] they require temperatures in excess of 200°. The fact that cleavage of V occurs readily at 80° suggests that the reaction may be of utility for the synthesis of acetylenes.

SCHEME I



Experimental Section[8]

Materials.—Carbomethoxymethylenetriphenylphosphorane (Ia) and cyanomethylenetriphenylphosphorane (Ib) were pre-

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[6] Phosphoranes IIa and b, on the other hand, were too highly colored for visual observation of thermochromism.

[7] (a) G. Märkl, *Chem. Ber.*, **94**, 3005 (1961); (b) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 2333 (1962); (c) P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *J. Org. Chem.*, **30**, 1015 (1965).

[8] Melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 137 Infracord in chloroform solution. Visible absorption spectra were obtained on a Cary 14 recording spectrophotometer.

pared according to Isler,[9] Trippett,[10] and co-workers, respectively. The benzene used in all runs was anhydrous.

α-(2,4,6-Trinitrophenyl)-α-carbomethoxymethylenetriphenylphosphorane (IIa).—A mixture of 2.01 g (0.0060 mole) of Ia and 0.74 g (0.0030 mole) of picryl chloride in 20 ml of benzene was heated on the steam bath for 1 hr. The phosphonium chloride, which was filtered off, washed with benzene, and dried, had a weight of 1.01 g (91%). The filtrate was evaporated to dryness and the residue was recrystallized from methanol–water to yield 0.93 g (57%) of violet-red crystals of phosphorane IIa: mp 192–193°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 493 mμ (ϵ 3930); infrared bands at 1640 (conjugated ester), 1604, 1538, 1490, 1440, 1342, 1302, 1250, 1102, 978, and 934 cm^{-1}.

Anal. Calcd for $C_{27}H_{20}N_3O_8P$: C, 59.45; H, 3.69; N, 7.70; P, 5.68. Found: C, 59.72; H, 3.90; N, 7.78; P, 5.45.

α-(2,4,6-Trinitrophenyl)-α-cyanomethylenetriphenylphosphorane (IIb).—A mixture of 4.00 g (0.0132 mole) of Ib and 1.64 g (0.0066 mole) of picryl chloride in 120 ml of benzene was heated on the steam bath for 2 hr. The phosphonium chloride was filtered off and weighed 1.93 g (87%). Evaporation of the filtrate and recrystallization of the residue from methanol yielded 1.77 g (52%) of violet-brown crystals of phosphorane IIb: mp 245–246°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 465 mμ (ϵ 12,300); infrared bands at 2180 (conjugated nitrile), 1606, 1589, 1540, 1491, 1440, 1330, 1266, 1100, 1090, and 963 cm^{-1}.

Anal. Calcd for $C_{26}H_{17}N_4O_6P$: N, 10.93; P, 6.04. Found: N, 10.51; P, 6.30.

α-(2,4-Dinitrophenyl)-α-carbomethoxymethylenetriphenylphosphorane (IIIa).—A solution of 2.01 g (0.0060 mole) of Ia and 0.61 g (0.0030 mole) of 2,4-dinitro-1-chlorobenzene in 40 ml of benzene was allowed to reflux for 70 hr under an atmosphere of nitrogen. The phosphonium salt was filtered off and weighed 0.52 g (47%). To the filtrate was added an equal volume of petroleum ether (bp 30–60°). The red precipitate that formed was filtered off to yield 0.84 g of solid, mp 210–220°. The product was slurried in a small amount of methanol, filtered, and dried. There was obtained 0.39 g (26%) of the orange-red phosphorane IIIa, mp 230–231°. An analytical sample was recrystallized from methanol–water and had mp 231–232°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 453 mμ (ϵ 9800); infrared bands at 1640 (conjugated ester), 1600, 1538, 1518, 1482, 1440, 1342, 1320, 1249, 1151, 1107, 1090, and 840 cm^{-1}.

Anal. Calcd for $C_{27}H_{21}N_2O_6P$: N, 5.60; P, 6.19. Found: N, 5.73; P, 6.50.

When the above reaction was carried out in 50 ml of dimethylformamide at 100° for 4 hr, followed by addition of water, extraction with benzene, precipitation with petroleum ether, and washing with methanol, 0.45 g (30%) of IIIa was obtained, mp 229–230°.

α-(2,4-Dinitrophenyl)-α-cyanomethylenetriphenylphosphorane (IIIb).—A solution of 10.00 g (0.0332 mole) of Ib and 3.35 g (0.0166 mole) of 2,4-dinitro-1-chlorobenzene in 200 ml of benzene was heated at reflux for 70 hr under an atmosphere of nitrogen. After cooling, the precipitate was filtered off, thoroughly washed with water to remove the phosphonium chloride, and dried. This material was recrystallized from benzene–petroleum ether and then from chloroform–methanol to yield 2.30 g (30%) of orange phosphorane IIIb: mp 249–250°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 437 mμ (ϵ 21,100); infrared bands at 2180 (conjugated nitrile), 1606, 1582, 1535, 1508, 1484, 1440, 1338, 1318, 1248, 1105, 960, and 832 cm^{-1}.

Anal. Calcd for $C_{26}H_{18}N_3O_4P$: N, 8.99; P, 6.63. Found: N, 8.78; P, 7.35.

2,4-Dinitrobenzylidenetriphenylphosphorane (IV).—A solution of 10.0 g (0.0383 mole) of 2,4-dinitrobenzyl bromide[11] in 20 ml of benzene was added over 5 min to 10.1 g (0.0385 mole) of triphenylphosphine in 200 ml of benzene. The mixture was allowed to stand for 16 hr whereupon the phosphonium bromide separated out as a gum. The benzene solution was decanted and the gum was washed with two 50-ml portions of hot benzene. Attempted crystallization of the salt was not successful. The gum was treated with five 200-ml portions of hot water in order to dissolve it. The water solution was filtered, cooled to 15°, and treated with a 2 *N* sodium hydroxide solution until slightly basic. The dark red solid which precipitated was filtered, washed thoroughly with water, and dried. Recrystallization from chloroform–petroleum ether afforded 7.88 g (46%) of the dark red phosphorane IV: mp 209–210°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 455 mμ (ϵ 36,600); infrared bands at 1612, 1560, 1502, 1482, 1441, 1374, 1350, 1309, 1267, 1140, 1114, 1102, 940, and 900 cm^{-1}.

Anal. Calcd for $C_{25}H_{19}N_2O_4P$: N, 6.33; P, 7.00. Found: N, 6.26; P, 7.25.

When phosphorane IV was recrystallized from benzene, a 1:1 complex between IV and benzene was formed.

Anal. Calcd for $C_{25}H_{19}N_2O_4P\cdot C_6H_6$: C, 71.53; H, 4.84; N, 5.38; P, 5.95. Found: C, 71.34; H, 4.72; N, 5.16; P, 6.04.

From the treatment of 1.00 g of IV with hot methanol was isolated 0.34 g (82%) of 2,4-dinitrotoluene and 0.48 g (76%) of triphenylphosphine oxide.

Reaction of Phosphorane IV with Methyl Chloroformate.—A mixture of 1.33 g (0.0030 mole) of IV in 10 ml of methyl chloroformate and 50 ml of benzene was refluxed under an atmosphere of nitrogen for 40 hr. The solution was decanted hot and the phosphonium chloride gum was washed with hot benzene. The combined benzene layers were evaporated to dryness. The residue was slurried twice with 25-ml portions of benzene and filtered. The dark red solid which was collected was starting material (identified by infrared and mixture melting point) and weighed 0.66 g (42% recovery as the 1:1 benzene complex). Petroleum ether (150 ml) was added to the filtrate and the precipitated solid was filtered off. Upon washing with a small amount of methanol, 0.17 g (23%) of an orange-red phosphorane was obtained, mp 228–230°. The infrared spectrum of this compound was identical with the infrared spectrum of IIIa and mixture melting point with IIIa showed no depression.

Reaction of Phosphorane IV with Benzoyl Chloride.—A mixture of 1.09 g (0.00246 mole) of IV and 0.18 g (0.00128 mole) of benzoyl chloride in 50 ml of benzene was refluxed under an atmosphere of nitrogen for 16 hr. The phosphonium chloride formed as a gum on the sides of the flask. The benzene was decanted and the gum was washed with hot benzene. The combined benzene solutions were evaporated to dryness. A yellow solid was obtained weighing 0.56 g. The infrared spectrum of this material was practically identical with the infrared spectrum of a synthetic 1:1 mixture of (2,4-dinitrophenyl)phenylacetylene (VII) (using the pure acetylene below) and triphenylphosphine oxide. On this basis the yield is 83% (theory requires a 0.67-g mixture of the two components). The mixture was recrystallized from 5 ml of methanol to give 0.17 g (51%) of pure acetylene VII, mp 117–118° (lit.[12] mp 112–112.5°).

Anal. Calcd for $C_{14}H_8N_2O_4$: N, 10.44. Found: N, 10.12.

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(10) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).

(11) S. Sugden and J. B. Willis, *ibid.*, 1360 (1951).

(12) P. Pfeiffer and E. Kramer, *Chem. Ber.*, **46**, 3655 (1913).

A Convenient Synthesis of 1-β-D-Arabinofuranosylthymine[1]

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The natural product, 1-β-D-arabinofuranosylthymine, isolated from a species of sponge (*Cryptotethia crypta*),[2,3] is the prototype of a series of arabinofuranosyl nucleosides given the trivial name "spongo" nucleosides. 1-β-D-Arabinofuranosylthymine (**5**) has been synthesized previously from synthetic 1-β-D-ribofuranosyl-