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

GUNTHER S. FONKEN

Biochemical Research Division, The Upjohn Company,
Kalamazoo, Michigan 49001

Received January 28, 1965

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), $\lambda_{\max}^{\text{EtOH}}$ 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°, $\lambda_{\max}^{\text{EtOH}}$ 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).

3,3,20,20-Bis(ethylenedioxy)-11α-(2-methoxyphenyl)-5β-pregnan-11β-ol.—2-Methoxyphenyllithium was prepared by the procedure of Gilman, *et al.*,[6] from 60 g. of 1-bromo-2-methoxybenzene and 200 ml. of 1.2 *M* ethereal butyllithium. To the aryllithium solution at 5° was added, over the course of 1 hr., a solution of 20.9 g. of 3,3,20,20-bis(ethylenedioxy)-5β-pregnan-11-one in 50 ml. of benzene and 150 ml. of ether. The mixture was stirred at room temperature overnight, and then washed several times with water, filtered through sodium sulfate, and evaporated to dryness. The crude material was dissolved in Skellysolve B and chromatographed over Florisil, from which the bulk of the material and all of the steroidal material was found in the 10% acetone–Skellysolve B eluate fractions. These were individually subjected to fractional crystallization from acetone–Skellysolve B to give 1.51 g. of 3,3,20,20-bis(ethylenedioxy)-11α-(2-methoxyphenyl)-5β-pregnan-11β-ol, m.p. 195–205°. The analytical sample was recrystallized from acetone–Skellysolve B: m.p. 203–206°; $[\alpha]^{20}\mathrm{D}$ +84° (*c* 1, acetone); $\lambda_{\max}^{\mathrm{EtOH}}$ 219 mμ (A_{m} 7225), 272 (1975), 279 (1900).

Anal. Calcd. for $C_{32}H_{46}O_6$: C, 72.97; H, 8.80. Found: C, 72.66; H, 9.40.

Hydrolysis of a 1.02-g.s ample of crude (m.p. 195–205°) 3,3,20,20-bis(ethylenedioxy)-11α-(2-methoxyphenyl)-5β-pregnan-11β-ol in 200 ml. of methanol containing 25 ml. of 1 *N* hydrochloric acid at room temperature overnight gave 0.91 g. of silky matted needles of **11β-hydroxy-11-(2-methoxyphenyl)-5β-pregnane-3,20-dione**, m.p. 191–201°. Recrystallization from acetone–Skellysolve B gave an analytical sample: m.p. 197–203°; $[\alpha]^{20}\mathrm{D}$ +135° (*c* 1, acetone); $\lambda_{\max}^{\mathrm{EtOH}}$ 271 mμ (A_{m} 1980), 278 (1920).

Anal. Calcd. for $C_{28}H_{38}O_4$: C, 76.67; H, 8.73. Found: C, 76.24; H, 8.73.

3,3,20,20-Bis(ethylenedioxy)-11α-(2-pyridylmethyl)-5β-pregnan-11β-ol.—The reaction between α-picolyllithium, prepared by the *Organic Syntheses*[7] procedure from 6.9 g. of lithium wire, and a solution of 20.9 g. of 3,3,20,20-bis(ethylenedioxy)-5β-pregnan-11-one in 100 ml. of benzene and 100 ml. of ether was carried out essentially as described for the pyridyllithium reaction. The crude product was eluted from a Florisil chromatogram by 25% acetone–Skellysolve B and was crystallized from methanol to give 13.44 g. of 3,3,20,20-bis(ethylenedioxy)-11α-(2-pyridylmethyl)-5β-pregnan-11β-ol, m.p. 148–152°. The analytical sample, recrystallized from methanol, had m.p. 154–156°, $[\alpha]^{20}\mathrm{D}$ −58° (*c* 0.8, acetone), $\lambda_{\max}^{\mathrm{EtOH}}$ 264 mμ (A_{m} 3775).

Anal. Calcd. for $C_{31}H_{45}NO_5$: C, 72.76; H, 8.86; N, 2.74. Found: C, 73.08; H, 9.32; N, 3.14.

Hydrolysis of 5.0 g. of 3,3,20,20-bis(ethylenedioxy)-11α-(2-pyridylmethyl)-5β-pregnan-11β-ol in 500 ml. of methanol containing 100 ml. of 1 *N* hydrochloric acid at room temperature overnight gave, after recrystallization from aqueous methanol, 2.68 g. of **11β-hydroxy-11α-(2-pyridylmethyl)-5β-pregnane-3,20-dione**, m.p. 167–172°. An analytical sample, m.p. 170–173°, was obtained after two recrystallizations from aqueous methanol: $[\alpha]^{20}\mathrm{D}$ −10° (*c* 1, acetone), $\lambda_{\max}^{\mathrm{EtOH}}$ 263 mμ (A_{m} 3875).

Anal. Calcd. for $C_{27}H_{37}NO_3$: C, 76.56; H, 8.81; N, 3.31. Found: C, 76.37; H, 9.06; N, 3.39.

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[6] H. Gilman, J. L. Towle, and S. M. Spatz, *J. Am. Chem. Soc.*, **68**, 2017 (1946).

[7] L. A. Walter, *Org. Syn.*, **23**, 83 (1943).

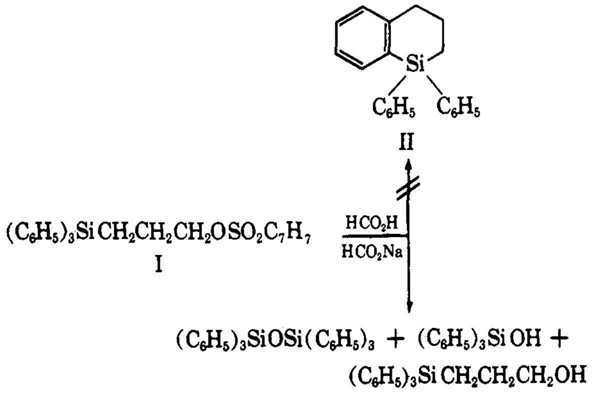
Reaction of Triphenylsilyllithium with *p*-Toluenesulfonates

HENRY GILMAN AND OREN L. MARRS

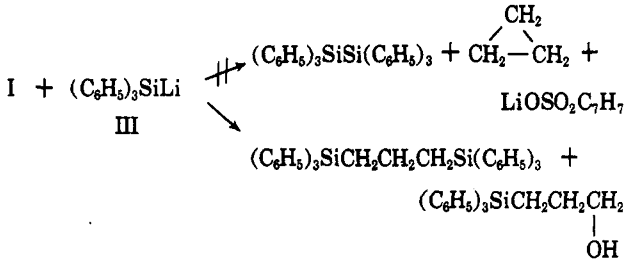
Department of Chemistry, Iowa State University, Ames, Iowa

Received September 15, 1964

In an attempt to prepare 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (II)[1] by a method Heck and Winstein[2] found applicable for the preparation of tetralin, 3-triphenylsilylpropyl *p*-toluenesulfonate (I) was prepared and subjected to formolysis. However, none of II could be isolated; hexaphenyldisiloxane, triphenylsilanol, and 3-triphenylsilylpropanol-1 were the major products. A trace of a solid melting at 81–82° was also obtained, but this was not II, allyl- or propenyltriphenylsilane. Since hexaphenyldisiloxane and triphenylsilanol are probably products of γ-elimination, it was postulated that triphenylsilyllithium (III) would react with I to give the highly insoluble hexaphenyldisilane *via* γ-elimination, a reaction previously observed between 3-bromopropyltrimethylsilane and aluminum chloride,[3] 3-bromopropyltrichlorosilane and base,[3] and heating 3-chloropropyldiethylmethylsilane.[4]



$(C_6H_5)_3SiCH_2CH_2CH_2OSO_2C_7H_7 \xrightarrow[HCO_2Na]{HCO_2H} (C_6H_5)_3SiOSi(C_6H_5)_3 + (C_6H_5)_3SiOH + (C_6H_5)_3SiCH_2CH_2CH_2OH$



However, in only one of three runs was hexaphenyldisilane isolated, and then in a low yield (5.6%). The preferred reaction appears to be a normal alkylation reaction as 1,3-bis(triphenylsilyl)propane[5] was obtained. When a 1:1 ratio of the silyllithium to the sulfonate was employed, a 41.6% yield of 3-triphenylsilylpropanol-1 was isolated along with the propane (34%). When 2 equiv. of III were added to 1 equiv. of the sulfonate I, the yield of the propanol was 9.4% and that of the propane was 53.5%. Other products were triphenylsilane (9.6%), tetraphenylsilane (2.5%), and triphenylsilanol (5.1%). The fact that 2 equiv. of III were required to give good yields of the propane derivative (almost 2 equiv. of VI were added before Color Test I[7] became positive) was surprising, as III

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[1] See, H. Gilman and O. L. Marrs [*J. Org. Chem.*, **29**, 3175 (1964); **30**, 1942 (1965)] for the synthesis and properties of these compounds.

[2] R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).

[3] L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, *ibid.*, **71**, 3056 (1949).

[4] V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev, and A. D. Petrov, *Proc. Acad. Sci. USSR, Chem. Sect.* (Eng. Transl.), **106**, 17 (1956).

[5] This compound has been reported [N. S. Nametkin, A. V. Topchiev, T. I. Chernusheva, and S. D. Durgar'yan, *Tr. Mosk. Neft. Inst.*, **22**, (1958); *Chem. Abstr.*, **53**, 18894 (1959)] to melt at 209.5–210°, but the compound has also been prepared from triphenylsilyllithium and 3-bromopropyltriphenylsilane and has been found to melt at 131–132°.

[6] H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 1107 (1959).

[7] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).