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A Facile Reduction of Ar_3COH to Ar_3CH

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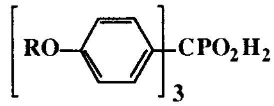
ABSTRACT

Modification of the conditions described for the preparation of triarylmethylphosphonous acids from hypophosphorous acid and triarylmethanols allows facile reduction of the C–O–H linkage to the C–H linkage. © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**:501–503, 1997

INTRODUCTION

In the course of our continuing efforts concerning the synthesis of ionic dendrimers [1], we set out to synthesize a series of tri(4-substitutedaryl)methylphosphonous acids **1** that could serve ultimately as branch points for the elaborated dendrimer species. Our approach toward the synthesis of these materials was based on the reported method of Hatt [2] using sodium hypophosphite and triphenylmethanol. In addition to the formation of the target material triphenylmethylphosphonous acid (no yield reported), a small amount of a reduced by-product, triphenylmethane, was also reported by Hatt.



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Other reports have been made of the reduction of triarylmethanols to triarylmethanes. Early reports by Fosse [3] refer to the condensation of triphenylcarbinol with hypophosphorous acid to yield "triphenylmethylphosphinous acid" ($Ph_3CPO_2H_2$) and triphenylmethane under several sets of conditions (no yield). A later report describes the direct conversion of the triarylmethanol to the triarylmethane using arcidane derivatives as hydrogen transfer agents, analogues of NADH [4]. While the yield is good in this procedure, it is accomplished only with relatively small amounts of material. A second method involves the photolysis of triarylmethylphosphonic acid salts [5]. This latter method generates the triarylmethylphosphonic acid by an initial reaction of the triarylmethanol with phosphorus trichloride, and subsequent photolysis produces the triarylmethane in low yield, proceeding through the intermediate triarylmethide anion.

While our efforts in this synthetic effort have yielded the desired series of **1** [6], we have also uncovered an approach that allows facile reduction of the C–O–H linkage to the C–H linkage for triarylmethanols and related species. This approach allows the reduction to be performed not only in good yield but also on a preparative scale. We herein report on the development of the reaction conditions for this facile transformation.

Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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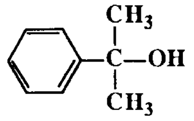
RESULTS AND DISCUSSION

Triarylmethanols **2** bearing moderately negative Hammett σ substituents in the *para* positions undergo rapid conversion to the corresponding triarylmethanes **3** upon heating in acetonitrile solution with 50% aqueous hypophosphorous acid (Scheme 1). The reaction appears to be dependent upon the formation of the triarylmethyl cation, as the unsubstituted triphenylmethanol undergoes reaction only under more stringent conditions involving longer heating times and the use of acetic acid as the solvent with added hydrochloric acid. Similarly, benzhydrol (**4**) undergoes reduction to diphenylmethane (**5**) in excellent yield with a higher hydrochloric acid component (Scheme 2).

Attempts to perform the analogous reduction on 2-phenyl-2-propanol (**6**) under the same conditions gave no reaction; the use of higher concentrations of hydrochloric acid resulted only in the formation of a mixture of alkene and alkyl chloride with little or no reduction. Similarly, attempts to reduce aromatic ketones using strongly acidic media resulted in the addition of the hypophosphorous acid across the carbonyl group.



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Given the reaction conditions, and their variation required for accomplishment of reduction with varying structure of the alcohol, we would propose that the reaction proceeds through hypophosphorous acid reduction of the carbocation with subsequent hydration of the oxidized phosphorus-containing species to form phosphorous acid (Scheme 3).

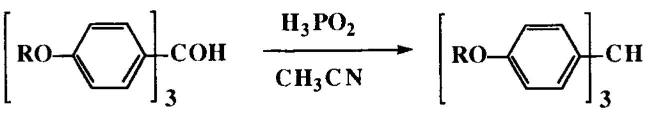
EXPERIMENTAL

General

All chemicals used in syntheses, purification, and comparison analyses were of commercial reagent quality and were used without purification. The following compounds were prepared according to previous reports: tri(4-methoxyphenyl)methanol [4], benzyl 4-bromophenyl ether [7], and methyl 4-benzyloxyphenylbenzoate [8]. Silica gel for preparative chromatography was obtained from EM Science (240–400 mesh). TLC determinations were performed using Kodak Chromagram silica gel sheets. All NMR spectra were measured using a Brüker 400 MHz DPX400 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of Tris(4-benzyloxyphenyl)methanol

To a solution of benzyl 4-bromophenyl ether (10.0 g, 38.0 mmol) in a mixture of diethyl ether (25 mL) and tetrahydrofuran (10 mL) was added magnesium turnings (1.0 g, 0.041 g-atom), and the mixture was heated at reflux with stirring for 12 hours. After that time, most of the magnesium metal had been consumed. The reaction mixture was cooled in an ice bath, and a solution of methyl 4-benzyloxybenzoate (5.00 g, 20.6 mmol) in a mixture of diethyl ether (50 mL) and tetrahydrofuran (20 mL) was added dropwise. Upon completion of the addition, the resultant red solution was heated at reflux for 3 hours, then cooled and neutralized by the addition of 0.5% hydrochloric acid. The organic layer was separated and dried over potassium hydroxide. After evaporation of the solvent, the viscous residue was purified by column chromatography (hexane/ethyl acetate 10/1 eluent) followed by recrystallization from diethyl ether to give the pure tris(4-benzyloxyphenyl)methanol (7.1 g, 65% yield) of mp 83–84°,



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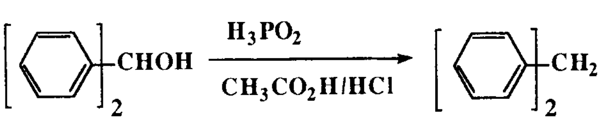
SCHEME 1



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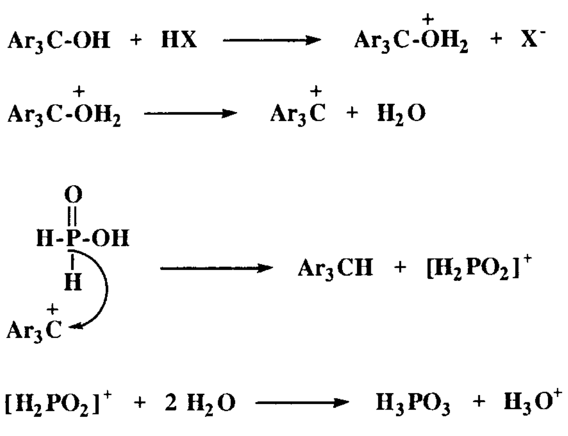
SCHEME 2



SCHEME 3

which exhibited spectra and elemental analyses in accord with the proposed structure. ^{1}H NMR (δ $CDCl_3$) 2.54 (1H, s); 5.04 (6H, s); 7.03 (12H, AA′BB′); 7.23–7.43 (15H, m). ^{13}C NMR ($CDCl_3$) 70.40, 81.50, 114.43, 127.90, 128.38, 128.99, 129.47, 137.35, 140.26, 157.59. Anal: $C_{40}H_{34}O_4$ requires: C, 83.02%; H, 5.92%. Found: C, 83.20%; H, 5.98%.

Reduction of Tris(4-benzyloxyphenyl)methanol to Tris(4-benzyloxyphenyl)methane

A solution of tris(4-benzyloxyphenyl)methanol (6.81 g, 11.8 mmol) in acetonitrile (45 mL) and hypophosphorous acid (4.76 g of 50% aqueous solution, 36.1 mmol) was stirred and heated at 60° for 6 hours. After that time, the solvent was evaporated under reduced pressure, and diethyl ether (10 mL) was added to the residue. The resultant solid was recrystallized from absolute ethanol to give the pure tris(4-benzyloxyphenyl)methane (4.8 g, 72.3% yield) of mp 115–116°, which exhibited spectra and elemental analyses in accord with the proposed structure. ^{1}H NMR (δ $CDCl_3$) 5.06 (6H, s); 5.43 (1H, s); 6.99 (12H, AA′BB′); 7.35–7.47 (15H, m). ^{13}C NMR ($CDCl_3$) 54.53, 70.13, 114.64, 127.63, 127.88, 128.05, 128.69, 137.12, 137.24, 157.32. Anal: $C_{40}H_{34}O_3$ requires: C, 85.37%; H, 6.09%. Found: C, 85.42%; H, 6.16%.

Reduction of Tris(4-methoxyphenyl)methanol to Tris(4-methoxyphenyl)methane

A solution of tris(4-methoxyphenyl)methanol [^{1}H NMR (δ $CDCl_3$) 2.80 (1H, s), 3.82 (9H, s), 7.02 (12H, AA′BB′); ^{13}C NMR ($CDCl_3$) 53.98, 79.87, 112.17, 127.70, 138.45, 157.28] (0.35 g, 1.03 mmol) in acetonitrile (10 mL) and hypophosphorous acid (0.312 g of 50% aqueous solution, 2.36 mmol) was stirred and heated at reflux for 2 hours. After that time, the solvent was evaporated under reduced pressure, and the residue was washed with aqueous potassium carbonate and extracted with diethyl ether. After evaporation of the solvent under reduced pressure, the residue crystallized on standing to give the pure tris(4-methoxyphenyl)methane (0.30 g, 89.8% yield), which exhibited spectra in accord with the structure and corresponded to that previously reported [3] ^{1}H NMR (δ $CDCl_3$) 3.40 (9H, s), 5.57 (1H, s), 7.04 (12H, AA′BB′). ^{13}C NMR ($CDCl_3$) 54.93, 55.08, 114.21, 130.88, 137.48, 158.80.

Reduction of Triphenylmethanol to Triphenylmethane

A solution of triphenylmethanol (0.50 g, 1.92 mmol) in glacial acetic acid (15 mL) with concentrated hydrochloric acid (0.1 mL) and hypophosphorous acid (0.50 g of 50% aqueous solution, 3.79 mmol) was stirred and heated at reflux for 24 hours. After that time, the mixture was poured into water (100 mL), and the resultant precipitate was collected by suction filtration and washed with water and air-dried to give pure triphenylmethane (0.40 g, 85.3% yield) that corresponded to authentic commercial material in all characteristics.

Reduction of Benzhydrol to Diphenylmethane

A solution of benzhydrol (0.50 g, 2.71 mmol) in glacial acetic acid (15 mL) with concentrated hydrochloric acid (0.5 mL) and hypophosphorous acid (0.71 g of 50% aqueous solution, 5.38 mmol) was stirred and heated at reflux for 24 hours. After that time, the solution was cooled and neutralized with aqueous potassium hydroxide solution. An upper organic layer formed and from it was isolated benzhydrol (0.15 g) and diphenylmethane (0.26 g, 81.1% yield), which corresponded to authentic commercial material in all characteristics.

ACKNOWLEDGMENTS

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