# Direct Chemical Reduction of Triphenylcarbinol to Triphenylmethane

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BH_3CN^- has been found to be a moderately efficient trapping agent for triphenylmethyl cations, roughly comparable to chloride ion. Since BH_3CN^- is moderately resistant to acid hydrolysis, it can trap triphenylmethyl cations generated by treatment of triphenylcarbinol with HCl in 25% water — 75% tetrahydrofuran. A quantitative yield of triphenylmethane, based on unrecovered triphenylcarbinol, can be obtained, but the process is inefficient in its use of BH_3CN^- because of the competing hydrolysis.

In the last few years cyanotrihydridoborate ion, BH_3CN^-, has found wide use as a borohydride type reducing agent which will tolerate moderate concentrations of acid.[2,3] Because of this property we thought it might be used to reduce tertiary alcohols to the corresponding hydrocarbons in acidic medium (eq. 1). Some further utilization of the remaining two

$$ROH + H^+ + BH_3CN^- \rightleftarrows RH + H_2O + BH_2CN \qquad (1)$$
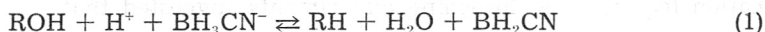
hydridic hydrogens of BH_2CN might also be expected.[2] These expectations have been realized for triphenylcarbinol, but under conditions which suggest that the procedure cannot be extended to alcohols which lead to less stable carbonium ions. For highly stabilized carbonium ions the method may sometimes provide a useful trap, especially since the hydrocarbons do not undergo further solvolysis, as do many other derivatives. It may also sometimes be a synthetically useful reduction, leading directly to the hydrocarbon. The unsubstituted anion, BH_4^-, is capable of directly reducing alkyl halides and sulfonate esters,[4,5] but not alcohols because of its sensitivity to acid.

In the course of this investigation triphenylmethyl chloride has also been reduced to triphenylmethane and BH_3CN^- has been placed on the Swain, Scott, and Lohmann scale of relative nucleophilicities.[6]

RESULTS AND DISCUSSION

All reactions were carried out in solvent mixtures containing 75% tetrahydrofuran (THF) and 25% water, by volume. This mixture was chosen because it dissolves both reagents and its organic constituent does not enter the reaction. Acetone, which was used by Swain, Scott and Lohmann,[6] would be reduced by BH_3CN^-. Alcohols would react with the carbonium ion. All reactions were carried out at room temperature which was always between 25 and 28 °C.

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To establish that relative nucleophilicities in this medium are comparable to those in acetone-water mixtures, the relative reactivity of azide ion and water were determined using eq. (2).

$$k_{N_3^-}/k^0 = \{[H_2O]/[Ph_3COH]_f\} \ln \{[N_3^-]_i/([N_3^-]_i + [Ph_3COH]_f - [Ph_3CCl]_i)\} \quad (2)$$

Eq. 2 was obtained by integrating eq. 3.[6] The integrated form of the

$$d[Ph_3CN_3]/d[Ph_3COH] = k_{N_3^-}[N_3^-]/k^0[H_2O] \quad (3)$$

equation had to be used because the high reactivity of N_3^- does not permit its use in large excess. Quantities in brackets in eqs. 2 and 3 are concentrations. Concentrations subscripted i are initial values and those subscripted with f are final values. To carry out the integration all concentrations except that of H_2O (which is effectively constant) were expressed as functions of time. A value of 1.4×10^5 was obtained. This compares very well with the value of around 2.5×10^5 which was reported[6] for various water-acetone mixtures.

Since BH_3CN^- proved to be much less reactive than N_3^- it was used in large excess. When BH_3CN^- was 0.08 M, reduction of triphenylmethyl chloride to triphenylmethane in 97% yield resulted. Using eq. 4, which is analogous to eq. 3, $k_{BH_3CN^-}/k^0$ could be determined. It was 5.3×10^3. This places

$$k_{BH_3CN^-}/k^0 = [Ph_3CH]_f[H_2O]/[Ph_3COH]_f[BH_3CN^-] \quad (4)$$

BH_3CN^- somewhat above acetate, below thiocyanate, and similar to chloride ion in its nucleophilicity toward the triphenylmethyl cation.[6]

In the presence of acid triphenylcarbinol is converted to the triphenylmethyl cation (eq. 5).[7] The foregoing experiments suggested that

$$Ph_3COH + H^+ \rightleftarrows H_2O + Ph_3C^+ \quad (5)$$
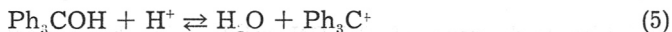
0.1 M BH_3CN^- (or less) should be sufficient to trap almost all the triphenylmethyl cation as it is formed. This was realized by reduction of 10 mmol of triphenylcarbinol to triphenylmethane in 28% yield during an eight hour period by a solution in which the BH_3CN^- was maintained at 0.1 M and the H^+ was kept at about 0.2 M. In the process about 30 mmol acid and 30 mmol of BH_3CN^- were consumed, most of the latter being hydrolyzed to borate and gaseous hydrogen. The unconverted triphenylcarbinol was all recovered unchanged (and presumably could have been carried further toward completion simply by prolonging the reaction time) so the process is potentially very efficient in terms of the alcohol but wasteful of the reducing agent. The nucleophilicity of BH_3CN^-, given above, suggests that a ten-fold reduction in loss to hydrolysis could be achieved with only a 30% reduction in alcohol conversion rate by reducing the BH_3CN^- concentration by a factor of 10.

At the electrolyte concentration used it is likely that a sizable fraction of the ions are paired in this solvent.[8] The nucleophilicity of the ions is probably reduced by such pairing. In addition, the cation may react while it is still under the influence of its counterion. Both of these factors suggest that the exact ratios of rate constants (and the yields that depend on them) are specific to the conditions under which they were measured.[9] It has been shown, however, that the ratio, $k_{N_3^-}/k^0$, is approximately independent of solvent, temperature, and (for the triphenylmethyl system) leaving group, over a fairly wide range.[6]

This suggests that the parameters presently reported will apply, with modest changes, to a fairly wide range of conditions.

EXPERIMENTAL

Triphenylcarbinol was obtained from Eastman Organic Chemicals and was recrystallized from ethanol; m. p. 164 ^{0}C. Triphenylmethyl chloride was prepared from triphenylcarbinol[10] and recrystallized from a mixture of dry benzene and petroleum ether. It had m. p. 108—112 ^{0}C (reported[6] 111.9—112.4 ^{0}C). Tetrahydrofuran was of reagent grade, from J. T. Baker Chemical Co., and was distilled before use. Sodium azide was obtained from Eastman Organic Chemicals, and was recrystallized from an acetone-water mixture. Sodium cyanotrihydridoborate was a gift of the Ventron Corporation and was used without further purification. Its hydride content was determined iodometrically,[11] assuming it has three available, hydridic, hydrogens. Hydrochloric acid was prepared by dilution of constant boiling acid.[12]

The two solvolysis reactions were carried out in the usual way[6] in 100 ml of solution initially containing, in each case, 0.28 g (1 mmol) of triphenylmethyl chloride and the requisite inorganic materials. In the product mixture from solvolysis in the presence of N_3^- the alcohol concentration was assumed to be equal to the acid concentration, and the latter was determined by titration. The product mixture from the solvolysis in the presence of BH_3CN^- was isolated by removing the tethrahydrofuran under vacuum, and extracting the organic products into CCl_4. When the CCl_4 was removed under vacuum, and the product recrystallized from ethanol, triphenylmethane, m. p. 92—94 ^{0}C (reported [13] 92 ^{0}C) was obtained, as white, needlelike crystals. The amount of alcohol in the product mixture was determined by comparing the intensity of the 2758 nm free OH band of the CCl_4 product solution with that of knowns, both in 1 cm quartz cells. The Beer-Lambert Law was shown to be obeyed up to concentrations of 10^{-2} M.

The reduction of the alcohol was carried out in 100 ml of solution, in a 250-ml 3-neck flask. The flask was with a combination glass electrode for measuring pH, a gas pressure release device to maintain a small positive pressure in the reaction flask, one burette filled with 5 M HCl, and one burette filled with 5 M $NaBH_3CN$. The relation between H^+ concentration and the reading on a conventional pH meter, in a mixed solvent with several solutes, is complicated, but at constant meter reading the H^+ concentration is constant. A solution, in this solvent, containing 0.2 M HCl and 0.1 M $NaBH_3CN$, was found to give a meter reading of 1.0. At this H^+ concentration the hydrolysis reaction and the alcohol reduction each consume a mole of H^+ for each mole of BH_3CN^- consumed. The H^+ concentration was maintained by periodic additions from the HCl burette to keep the pH reading constant. Each time HCl was added a similar quantity of $NaBH_3CN$ was added, maintaining its concentration at a constant level also.

The products were isolated as described for the solvolysis reaction in the presence of BH_3CN^-. The recovery of triphenylmethyl compounds was quantitative. In this case, since the alcohol : hydrocarbon ratio was not too far from one, analysis by NMR spectra were recorded in approximately 1 M solutions in dry CCl_4 at about 35 ^{0}C. of the peak due to the aliphatic proton of triphenylmethane (5.5 ppm downfield from tetramethylsilane) with the area of the peak due to the hydroxylic proton of the triphenylcarbinol (2.2 ppm downfield from tetramethylsilane). The relevant NMR spectra were recorded in approximately 1 M solutions in dry CCl_4 at about 35 ^{0}C.

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IZVOD

Direktna kemijska redukcija trifenilkarbinola u trifenilmetan

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Nađeno je da je BH_3CN^- umjereno sredstvo za hvatanje trifenilmetil kationa. Po svojoj efikasnosti može se usporediti s klorid ionom. Budući da je BH_3CN^- dosta otporan na kiseline, mogu se hvatati kationi dobiveni obradom trifenilkarbinola s HCl u 75⁰/₀ vodenom tetrahidrofuranu. Na taj način dobije se kvantitativno trifenilmetan, računajući prema potrošenom alkoholu. Čitav proces nije jako efikasan s obzirom na upotrebljenu količinu BH_3CN^- zbog konkurentne hidrolize.

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