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METAL-ASSISTED REACTIONS. PART 24.[1] THE IMPORTANCE OF SOLVENTS IN LIQUID-PHASE HETEROGENEOUS CATALYTIC TRANSFER REDUCTION

By

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In liquid-phase catalytic transfer reduction in which a hydrogen donor is used to effect hydrogenation of a substrate, reaction often proceeds sluggishly in single phase solvents but goes rapidly in biphasic solvent systems in which the catalyst usually resides in one or other of the phases. Depending on the nature of the substrate and donor, an excess of either can lead to the catalyst surface becoming saturated with one component, thereby preventing reaction. It is shown that the biphasic solvent system is, in practice, a simple means of controlling access to the catalyst by either the substrate or donor such that both are present on the surface in comparable amounts, leading to optimum or near optimum reaction rates.

Liquid-phase heterogeneous catalytic transfer reduction is becoming of increasing importance as an alternative to catalytic reduction with molecular hydrogen, particularly for large-scale industrial processes. The transfer method usually requires simple apparatus or industrial plant and does not present the hazards of gaseous hydrogen. Also, the degree of selectivity by transfer methods is frequently better than that offered by standard reduction with hydrogen and a catalyst.[2] For example, aromatic nitro compounds could be reduced to hydroxylamines in good to excellent yields by transfer methods in cases in which it had not been possible to synthesise them at all, either with molecular hydrogen and a catalyst or through the use of standard dissolving metal reduction.[3] Despite these advantages, transfer hydrogenation sometimes fails where reduction with a catalyst and molecular hydrogenation is successful as, for example, in attempted reduction of acid chlorides to aldehydes.[2] Whilst such failure has been ascribed to catalyst poisoning, in fact, very little fundamental knowledge is available on mechanisms of heterogeneous catalytic transfer reduction. In the recent past, a number of publications has approached this problem. Thus, transfer hydrogenation has been examined for aryl halides,[4-5] nitroarenes,[6] and aryloxytetrazoles[7] and it is becoming clear that transfer hydrogenation is not simply a conversion of hydrogen donor into molecular hydrogen

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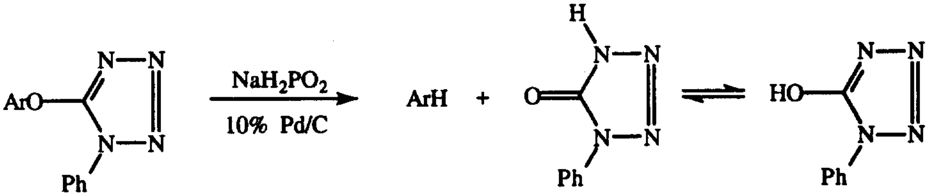
followed by "normal" hydrogenation but involves the transfer of hydrogen from the donor to the substrate on the catalyst surface.[6-7]

For the specific hydrogenolysis of tetrazolyl ethers of phenols (1) to give arenes (2; Scheme 1), incorporation of hydrogen has been shown to be so site specific that



1 2 3

SCHEME 1

it is an excellent method for introducing deuterium or tritium into a specific position in a benzene ring.[8] The reaction is characterised by burst kinetics in which a steady-state is attained and is controlled by the rate of release of the other reaction product, the phenyltetrazolone (3; Scheme 1).[7] There is no free energy relationship (Hammett correlation) between overall reaction rate and substituents in the aryloxy ring which also indicates that oxidative addition of the aryloxytetrazole to the catalyst cannot be rate-controlling for a wide range of substituents.[9]

Usually, this hydrogenolysis (Scheme 1) is rapid and high– yielding but only when carried out in a biphasic solvent system (toluene/water) in which the heterogeneous catalyst (Pd/C) floats in the upper organic phase, the substrate is dissolved in the same layer and the hydrogen donor (sodium phosphinate) is mostly in the aqueous layer. In a one-phase solvent system (e.g., with formic acid as solvent and hydrogen donor or with hydrazine in an organic solvent), reaction is sluggish and yields are not as good as with the two-phase solvent system.

A major problem in understanding the meaning of reaction rates in such a heterogeneous mixture of solid catalyst and two immiscible solvents lies in deciding on the effective concentrations of substrate and hydrogen donor with respect to the catalyst surface. For transfer reduction, the usual hydrogen donors (formic acid, formates, hydrazine, phosphinic acid and so on) are very soluble in water so that, in a biphasic solvent system with water as one phase, it is likely that most of the donor remains in the water. Therefore, in order to measure reaction rates in a one-phase organic solvent system, tetra-n– butylammonium phosphinate (TBP) and tetra-n-butylammonium formate (TBF) were synthesised; these donors are fully soluble in such solvents as toluene, ethanol and water. On attempted hydrogenolysis of a naphthoxytetrazole (Scheme 1) in a single solvent (toluene) with TBP and Pd/C catalyst, no reaction was observed, in stark contrast to the biphasic water/toluene solvent system. The work presented here highlights reasons for this contrasting behaviour and suggests ways in which it could be used to enhance the scope of heterogeneous transfer reduction.

RESULTS AND DISCUSSION

(a) **Solvent systems** - Benzene saturated with water and EtOH was used as a single-phase solvent; the water is necessary for the conversion of phosphinate into phosphite:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2[H]$$

As a test of the ability of TBP to act as a reducing agent, it was refluxed with nitrobenzene and 10% Pd/C in wet benzene for 5 hr when it gave complete reduction to aniline. Under similar conditions, aryloxytetrazole (4 = 1 in Scheme 1, where Ar = 2-naphthyl) was not reduced. In a biphasic solvent system of benzene/water/ethanol and TBP and 10% Pd/C, nitrobenzene was again reduced but the naphthoxytetrazole was not hydrogenolysed. However, with sodium phosphinate (NAP) as hydrogen donor, the biphasic solvent system was effective for reduction of both nitrobenzene and naphthoxytetrazole. In all the experiments, the catalyst remained in the organic layer. Both TBP and NAP contain the active hydrogen donor (phosphinate anion) but only TBP prevents reduction of the naphthoxytetrazole in both mono-and biphasic solvents. Consideration of the solubility properties of TBP and NAP suggested that, in the monophasic solvent, TBP is soluble and gives a high concentration of phosphinate whilst NAP is almost insoluble. In the biphasic solvent system, again TBP is likely to effectively provide more phosphinate anion in the upper organic layer than would NAP either because of a changed partition coefficient or because of a looser ion pair.[10] Thus, even in the biphasic system, the effective concentration of phosphinate would be higher in the organic layer for TBP than for NAP. If phosphinate is adsorbed on the catalyst surface more strongly than is the aryloxytetrazole but less so than the nitrobenzene, the above conflicting results can be rationalised in terms of competitive adsorptions of substrate and hydrogen donor onto the catalyst surface and their concentrations in solution. Thus, for NAP in the biphasic system, its solubility (concentration) in the upper benzene layer would be very small and therefore, even with a stronger adsorption of phosphinate onto the catalyst compared with that of the aryloxytetrazole, its effective surface concentration would be kept low and enable the aryloxytetrazole to adsorb also. Reduction with TBP does not occur because, even in the biphasic system, TBP provides too much phosphinate anion in the upper organic phase (which also contains the Pd/C catalyst), thereby giving a high concentration of phosphinate on the catalyst surface and preventing adsorption of the aryloxytetrazole. A series of experiments designed to test these conclusions was carried out:

Reactions of sodium phosphinate (NAP) in the monophasic solvent system.

When the naphthoxytetrazole (4) was dissolved in benzene (saturated with water) and stirred with solid NAP and 10% Pd/C, hydrogenolysis to naphthalene occurred such that the yield reached 50% in three hours. When a small (trace) quantity of 18-crown-6 (a weak complexer for Na^+) was added in a similar separate experiment, the yield reached 80% in the same time but, when 1.4 equivalents of crown ether (to NAP) were added, the same sort of experiment gave only a 33% yield of naphthalene in 3 hours. There was a maximum in yield and rate as the solubility of NAP in wet benzene was increased by addition of crown ether. Beyond a certain point, the increasing concentration of phosphinate in the organic layer appears to lead to its over-competitive adsorption onto the catalyst surface in preference to the aryloxytetrazole.

In a similar experiment, phosphinate anion was carried into a water-saturated benzene monophasic solvent from solid NAP by addition of phenyltrimethylammonium hydroxide. Again, hydrogenolysis proceeded at a reasonable rate if the amount of the phase transfer catalyst was kept small. This result is also important in that it suggests that a quaternary ammonium cation is not responsible for preventing hydrogenolysis and that there must be some other reason for the cessation of reaction with TBP.

Finally, in this series of qualitative reactions designed to limit the concentration of phosphinate in a monophasic solvent system, an experiment was carried out in which the naphthoxytetrazole (4) in benzene with 10% Pd/C catalyst was placed in the boiling flask of a liquid-liquid extractor; a solution of NAP in water was placed in the extraction flask. As the benzene boiled, was condensed and flowed through the extraction flask and back to the boiling flask, the wet benzene returned with a small concentration of NAP. As the benzene began to return, hydrogenolysis started and then proceeded steadily but slowly; even after nine hours, there was still some starting tetrazole remaining, in contrast to the mere fifteen minutes reaction time required in a water/benzene biphasic system.

Reactions of tetrabutylammonium phosphinate (TBP) in the mono- and biphasic solvent systems

As reported above, TBP in both mono- and biphasic solvents gave no reduction of aryloxytetrazoles, although it would effect the reduction of nitrobenzene to aniline. In view of the experiments described in which the concentration of phosphinate anion was kept low but steady in the organic phase thereby allowing hydrogenolysis to occur, it appeared that TBP provided too high a concentration of phosphinate in both mono- and biphasic systems. In benzene saturated with water, the TBP is totally soluble, unlike NAP which remains largely undissolved. In a simple test of this hypothesis regarding concentration of phosphinate anion, a solution (10 ml)of 5-(4-methoxyphenyl)-1-phenyltetrazole in benzene (10^{-3} M) was stirred with 100 mg of 10% Pd/C catalyst. By observation of its uv absorption at 286 nm, it was found that 43% of the tetrazole was adsorbed onto the catalyst. When TBP (0.2 g: 0.65 mmole) was added to the solution, all of the aryloxytetrazole desorbed from the catalyst, demonstrating the stronger adsorption of phosphinate onto the catalyst surface.

In a quantitative experiment, aliquots of a solution of naphthoxytetrazole (4) in benzene were stirred with different amounts of 10% Pd/C catalyst; adsorption of the catalyst onto the catalyst was measured by uv spectroscopy at 286 nm. A graph of the amount of tetrazole adsorbed with increasing amounts of catalyst is shown in the Figure. Any equations concerning this graph are given in the Appendix. For small amounts of catalyst, the first part of the graph is linear and affords an estimate of the effective area occupied by the aryloxytetrazole on the palladium surface (Appendix). The results provide a value for the stability constant (K_s; strength of adsorption; Appendix) as being 3.1 x 10^5 ℓ.mole^{-1}, v.i.z., the naphthoxytetrazole was quite strongly adsorbed. Thus, the stability constant (K_D)

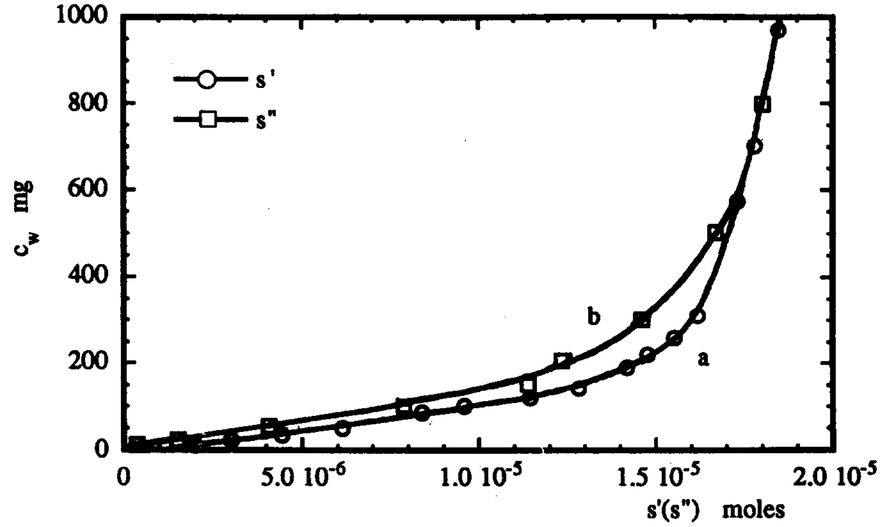


Figure. Variation in adsorption (s', s") of naphthoxytetrazole (4) onto different weights of 10% Pd/C catalyst (c_w) in benzene at room temperature in,(a) the absence of (s') and, (b) the presence of (s"), TBP.

for adsorption of phosphinate onto the catalyst must be somewhat greater than K_s since phosphinate displaces naphthoxytetrazole from the catalyst surface.

In a final demonstration that the concentration of phosphinate anion in the solvent phase containing the catalyst is important for hydrogenolysis (Scheme 1) to succeed, a solution of naphthoxytetrazole (4) in a water-saturated benzene (monophasic) solution was reacted with phosphinate by slow dropwise addition of a solution of TBP in benzene. The phosphinate was added over a period of thirty minutes when hydrogenolysis to naphthalene occurred. Therefore, unlike the experiments in which TBP was added at the beginning of reaction, giving a high initial concentration of phosphinate and no reduction, by keeping to a low level of the hydrogen donor, hydrogenolysis did proceed.

CONCLUSIONS

The above results indicate clearly that the concentration of hydrogen donor influences the outcome of heterogeneous catalytic transfer reduction. Where both donor and substrate molecules must be present on the catalyst surface at the same time for hydrogen transfer to occur, a high surface density by one or other of them will lead to a slowing of reaction and even a cessation in cases where the donor or substrate is adsorbed strongly enough to exclude the other. The adsorption or stability constant for binding at the catalyst surface is quite high for aryloxytetrazoles but that of phosphinate anion is greater. Therefore, to offset the stronger binding, the concentration of phosphinate anion must be reduced sufficiently or the amount of catalyst must be increased in order to leave some sites free for the substrate to adsorb. Presumably, the fastest reactions occur where the surface densities of substrate and donor are similar. The aqueous/organic solvent biphasic system with NAP has the advantage of keeping the concentration of phosphinate anion low in the organic layer where the catalyst resides. TBP, with its solubility in both water and organic solvent and its ability ot provide "naked" phosphinate anion, clearly gives too high a concentration of phosphinate anion in the catalyst/organic phase of both a monophasic and a biphasic system and prevents reduction.

For aromatic nitro compounds, TBP and NAP in mono- or biphasic solvent systems act as satisfactory hydrogen donors, presumably because nitro compounds bind as strongly or more strongly to the catalyst surface than do the aryloxytetrazoles and can compete with adsorption of phosphinate anion. In this respect, it is noteworthy that aromatic nitro compounds are reduced sluggishly in neat formic acid which is both a solvent and a hydrogen donor but, with biphasic formate/water/organic solvent systems, reduction is usually rapid.[11] By choice of hydrogen-donor and solvent or catalyst, reduction of aromatic nitro compounds to hydroxylamines can be controlled.[7] Perhaps this control lies in a stronger adsorption by the nitro compound but weaker adsorption of hydroxylamine to the catalyst surface compared with that of the hydrogen donor.

These results suggest that a better understanding of heterogeneous liquid phase catalytic transfer reduction will come through consideration and measurement of adsorption or binding constants of both substrate and donor to the catalyst surface, together with adjustment of their solution concentrations to equalize their surface densities on the catalyst surface, through suitable choice of solvent or delivery system.

APPENDIX

The information in the Figure was interpreted as follows. Let K_s be the stability or binding constant of the substrate (S) to be reduced and that, in the absence of donor, the equilibrium (2) can be written. In expressions (2,3),

$$\begin{array}{llll} & S + & Cat \rightleftharpoons & S.Cat^* \\ \text{Initially:} & s & c_w & - \\ \text{At equilibrium :} & s-s' & c_w-c_s' & c_s' \end{array} \qquad (2)$$

$$K_s = \frac{c_s'}{[s-s'](c_w-c_s')} \qquad (3)$$

c_w is the weight of catalyst (Cat) used, s is the initial concentration of substrate, s' is its "concentration" adsorbed onto the catalyst and c_s' is the area of metal surface occupied by substrate (nominally, $s' = c_s'$, after allowing for units of measurement). Equation (3) can be rearranged to give (4) and, when K_s is large and s' small (as when c_w is small), then the expression (4) can be simplified to (5). Therefore, for small amounts of catalyst,

$$c_w = c_s'\{(1/K_s[s-s']+1\} \qquad (4)$$

$$1/K_s[s-s'] \rightarrow o$$

$$c_w \simeq c_s' = s' \qquad (5)$$

the relationship between c_w and s' should be linear, as found in the Figure. The units for c_w and s' must be made the same. Clearly, the area of metal surface must be important and can be measured. For 10% Pd/C as used here, the dispersion of palladium is such as to give an area of 23 m^2/g of catalyst.[12] Multiplying c_w(mg) by 0.023 gives the metal area. For the area of substrate adsorbed onto the catalyst surface, s' must be multiplied by Avagadro's number (N) and by the area/molecule (a) of substrate. In these circumstances, equation (6) can be written. The graph (Figure) can be interpreted.

$$c_w(\text{mg}) = \frac{N.a.s'}{0.023} \;(\text{moles}) \qquad (6)$$

For the linear portion in the range $0 \leq c_w \leq 100$ mg, the slope is 1.23×10^7 mg/mole. Using equation (6), the area/molecule (a) is calculated to be 38×10^{-20} m^2. By assuming that the naphthoxytetrazole (4) used in this experiment is flat, an area/molecule of about 70×10^{-20} m^2 can be estimated from molecular modelling. However, molecular modelling also shows that, if the naphthyl part of the molecule lies flat on the surface (see below), then the tetrazole part must project upwards away from the surface and the effective area/ molecule on the surface is then estimated as about $30 - 40 \times 10^{-20}$ m^2. The agreement between the estimated and measured area/molecule is remarkable whether or not it is considered to lie flat on the surface or whether it lies with only the naphthyl part flat to the surface.

By using the experimental area/molecule, K_s can be calculated from equation (3) and the remaining points on the Figure in the region of slow steady change and large c_w. From these points, K_s was estimated to be approximately 3.1×10 ℓ.mole^{-1}. The second curve (b) in the Figure requires some comment. To assess the effect of phosphinate anion on the adsorption of the substrate to the catalyst surface, the above experiments were repeated, but this time adding a constant amount of hydrogen-donor to each solution of the substrate. The new adsorption of substrate (s") was measured and plotted against c_w. Comparison of the two curves (a,b) in the Figure reveals that they are very similar, beginning as two linear portions, a constant difference apart and eventually coalescing as c_w becomes large.

If the catalyst surface is fully covered by substrate and donor in the ratio, 1:r, ($r = d.K_D/s.K_s$; d is the concentration of donor with stability constant, K_D) then, in the absence of donor, $s' = c_w$ (equation 5) but, with donor present, $s'' = c_w(1/(1+r))$. From these expressions, equation (7) can be

$$s'-s'' = c_w(r/(1+r)) \qquad (7)$$

obtained by subtraction. For r = 0 (no donor), this reduces to $s' = s''$, as it should. For r = 1, $s'-s'' = c_w/2$, v.i.z., the catalyst surface is half covered by substrate and half by donor. This condition should give a near maximum rate of reaction. [Note, in the case of NAP, K_D is large but d is small so that r is small but for TBP, K_D is large and so, if d is large, so too is r. For large r, $s'-s'' = c_w$ or $s'' \simeq s'-c_w$. However, $c_w \simeq s'$ and so $s'' \simeq s'-c_w = 0$, v.i.z., all of the substrate is kept off the surface by the hydrogen donor and no reaction occurs. In the present experiments, a small quantity of donor was used ($d<<s$). Thus, $s' = c_w$ initially (equation 5) but, with K_D large, on addition of donor an equivalent of the substrate must desorb so that, $s'' = c_w - c_d$, where c_d is the amount of catalyst occupied by the donor. Therefore, $s'-s'' = c_w - (c_w - c_d) = c_d$. Since c_d is constant (d constant and K_D large) then, $s'-s'' = c_d$ = constant, i.e. there must be a constant difference between the curves (a,b) of the Figure over the early linear region where the catalyst surface is completely covered. In fact, examination of the values for $s'-s''$ for the range $0 \leq c_w \leq 40$ mg shows that $s'-s'' = (1.8 \pm 0.06) \times 10^{-6}$ mole. From the area/molecule for the naphthoxytetrazole (4) estimated above (38×10^{-20} m^2), this gives 0.43 m^2 as the area of substrate desorbed by the TBP donor (1.3×10^{-6} mole) and an area/ molecule for the donor of 53×10^{-20} m^2. Thus, the effective area of the donor on the catalyst surface is bigger than that of the naphthoxytetrazole and indicates that the tetra-n-butylammonium ion (large) associated with the phosphinate anion (small) must effectively keep a relatively large area of catalyst surface free from further adsorption by either donor or substrate. This experiment also indicates that the adsorption constant for the TBP (K_D) must be much greater than that of the substrate, (K_s). As described above, in the linear portion of the curves (a,b) of the Figure, $r = d.K_D/s.K_s$. From the curves (at c_w = 40 mg), $r = 1.5$, $d = 1.3 \times 10^{-6}$ mole, $s = 1.9 \times 10^{-6}$ mole and so, $K_D/K_s = 20$, v.i.z., the adsorption constant, K_D, for the donor must be at least twenty times greater than K_s. The result is consistent with the observed effect of TBP on the hydrogenolysis of aryloxytetrazoles. This aspect of the work will be reported more fully but it could be noted here that K_s for a 5—alkoxy-1-phenyl-tetrazole (1; Ar replaced by alkyl) is very much smaller than that of an aryloxytetrazole, indicating that the strong binding of the aryloxytetrazole is associated with the aryl group and not the tetrazole part.

EXPERIMENTAL

The synthesis of aryloxytetrazoles has been reported[3,7]; m.p.'s are not corrected. UV spectra were recorded on a Hewlet-Packard HP 8452A diode array spectrophotometer. GC results were obtained on a Dani 3800 gas chromatograph, using an OV351 capillary column. Hplc was performed on a Varian 5000 liquid chromatograph, using a C-18 reverse phase 10μ-Bondapak column with UV detection at 286 nm and methanol as eluant. Mass spectra were recorded on a VG 7070E mass spectrometer by EI at 70eV. In all experiments, only one batch of Pd/C catalyst (Lancaster Synthesis) was used.

Tetra-n-butylammonium salts

Tetra-n-butylammonium formate (TBF) was prepared from tetra-n-butylammonium hydroxide and an equivalent of formic acid in water.[13] Similarly, tetra-n-butylammonium phosphinate (TBP) was prepared by mixing aqueous solutions of tetra-n-butylammonium hydroxide and an equivalent of phosphoric acid (final pH7). The excess of water was evaporated on a rotary evaporator under water-pump vacuum to give colourless crystals, m.p. 52°C. This product (TBP) was extremely deliquescent and therefore difficult to analyse for C, H, P but gave reactions typical of phosphinate (reduction of $CuSO_4$) and gave an ion at m/z 242 ($C_{16}H_{36}N^+$).

Preparation of benzene/ethanol/water solvent. In all single solvent phase reductions a benzene/ethanol/water azeotrope (upper layer; 86: 12.7: 1.3%)[14] was used (B/E/W).

Hydrogenations in a monophasic solvent system

(a) Reduction of nitrobenzene with TPB. To a refluxing solution of nitrobenzene (790 mg) in benzene (10 ml) containing Pd/C catalyst (10% w/w; 194 mg) was added TPB (3 g) in B/E/W azeotrope (5 ml) and refluxing was continued for 5 hr after which the nitrobenzene had been reduced to aniline.

(b) Attempted reduction of naphthoxytetrazole (4). To a vigorously stirred refluxing solution of the naphthoxytetrazole (126 mg) in benzene (20 ml) containing Pd/C catalyst (10% w/w; 80 mg) was added TPB (200 mg) in B/E/W azeotrope (20 ml). After 20 hr. no reaction was observed.

(c) Reduction of naphthoxytetrazole (4) with controlled amounts of phosphinate.

(i) TBP. To a stirred, refluxing solution of the tetrazole (20 mg; 0.07 mmole) in B/E/W azeotrope (10 ml) containing Pd/C (10% w/w; 100 mg) was added dropwise over 20 min by syringe pump a solution of TBP (31 mg) in B/E/W (2 ml). Reduction to naphthalene was followed by tlc. The reaction went almost to completion in 3 hr. When the experiment was repeated but with dropwise addition of TBP over a period of 3 hr, the reaction proceeded at about the same rate.

(ii) NAP with 18-crown-6 ether. A stirred solution of the tetrazole (4; 44 mg) in B/E/W (40 ml) containing Pd/C catalyst (10%; 25 mg) and solid NAP (40 mg) was refluxed and the formation of naphthalene was followed by gc; after 3 hr, a 50% yield was obtained. The same experiment was carried out twice more but with the addition also of 18-crown-6 ether (8.1 mg in the first case and 32 mg in the second); the yields of naphthalene in 3 hr were respectively 80 and 33%.

(iii) NAP with phenyltrimethylammonium hydroxide. A stirred solution of the tetrazole (4; 39 mg) in B/E/W (20 ml) containing Pd/C catalyst (10%; 23 mg), phenyltrimethylammonium hydroxide (6.1 mg) and solid NAP (38 mg) was refluxed. Naphthalene was slowly formed, as shown by tlc.

(iv) NAP and liquid/liquid extraction. A solution of tetrazole (4; 45 mg) in benzene (80 ml) was placed in the "boiler" of a liquid/liquid extractor and a solution of NAP (1200 mg) in water (25 ml) was placed in the extraction thimble. As the benzene extracted small amounts of NAP from the thimble, reduction to naphthalene occurred slowly such that, after 19 hr, some starting material remained.

<u>Hydrogenations in a biphasic solvent system</u>

(a) Reduction of nitrobenzene with TBP. A mixture of nitrobenzene (17 mg) in benzene (10 ml) and TBP (1 g) in water (9 ml) with Pd/C catalyst (10%; 50 mg) was stirred and refluxed for 5 hr to give a 100% yield of aniline (tlc).

(b) Attempted reduction of tetrazole (4) with TBP. Similarly to (a), a solution of the tetrazole (40 mg) in benzene (10 ml) with TBP and catalyst gave no naphthalene after 30 hr. Only unchanged starting material was observed (tlc).

(c) Reduction of tetrazole (4) with NAP. This experiment was carried out as for (b) but with the use of NAP in place of TBP as hydrogen donor. A 100% yield of naphthalene was observed in 15 min.[7]

<u>Quantitative adsorption of tetrazoles onto Pd/C catalyst</u>

(a) A solution of 5-(4-methoxyphenyl)-1-tetrazole (1.085 x 10^{-5} mole) in benzene (10 ml) was stirred at room temperature (~20°C) with Pd/C catalyst (10%; 100 mg) for 1 hr. After settling, the supernatant liquid was filtered and its uv absorption at 286 nm was measured and compared with that of a standard solution; the drop in absorbance showed that 43% of the tetrazole (4.6 x 10^{-6} moles) had adsorbed onto the catalyst. The filtrate was returned to the still (solvent) wet catalyst and stirred; TBP (200 mg; 6.5 x 10^{-4} mole) was added. After 5 min, the uv absorption was again measured and showed that all of the adsorbed tetrazole had been desorbed into solution.

(b) A solution of the naphthoxytetrazole (4; 136.8 mg) in benzene (500 ml) was prepared. Aliquots (20 ml; 1.9 x 10^{-5} mole) were stirred with known weights of Pd/C catalyst (10%; 10.1 up to 970.1 mg - see Figure) for 1 hr. After settling, the supernatant liquid was filtered and its content of tetrazole was measured from peak areas at 286 nm after hplc and comparison with standard solutions. The change in peak area gave the amount of tetrazole adsorbed onto the catalyst (s' in the Figure).

In a similar series of experiments, a solution of naphthoxytetrazole (4; 68.6 mg) in benzene (250 ml) was prepared but also contained TBP (200 mg; 6.5 x 10^{+4} mole). Aliquots (20 ml) of this solution were stirred with known weights of Pd/C catalyst (10%; 10.9 up to 1009.3 mg - see Figure) for 1 hr and the adsorption of tetrazole was measured from hplc peak areas, as above. Changes in peak area gave the amount of tetrazole adsorbed onto the catalyst (s" in the Figure).

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