J. Org. Chem. **1989**, *54*, 949-953

spectrum is in accord with the reported literature data.

General Procedure for Oxidation of Alkynes. In a typical run, 2 mL of a solution of the desired alkyne (3 mmol) in DCE was added to a dichloroethane/water solution (13 mL) containing tris(cetylpyridinium) 12-molybdophosphate or 12-tungstophosphate (150 mg, ≈0.13 mmol), $Hg(OCOCF_3)_2$ (0.8 mmol), and hydrogen peroxide (20.5 mmol) under vigorous stirring in a glass reactor maintained at 40 °C. The alkyne is added as the last reagent, following the hydrogen peroxide addition, to minimize the formation of products arising from the hydration of the triple bond. At the end of the reaction, the two phases were separated and the organic phase was analyzed by GC-MS.

As an example of the preparative procedure, the isolation of the reaction products, included the carboxylic acids, from the reaction mixture is reported. In this case at the end of the reaction, the two phases were separated in a separatory funnel. The aqueous layer was acidified by H_2SO_4 at pH ≈ 1 and extracted with ethyl ether. The ethereal extract was joined to the organic phase and the resulting solution was dried on Na_2SO_4 and reduced to a small volume by solvent evaporation. The products in the organic phase were isolated by column chromatography (silica gel, cyclohexane–ethyl acetate, 9:1, or petroleum ether–diethyl ether, 8:2) and identified by comparison with authentic samples and by their ^{1}H NMR, IR, and mass spectra.

The yields of products were determined by quantitative GLC analysis (internal standard) using a 3% OV-17 on 80/100 Supelcoport column, with a Shimadzu Chromatopac C-E1B integrator and only for 1-hexyne an 80/100 Carbopack C/0.1% SP-1000 column with a Hewlett-Packard 5890A instrument equipped with a Perkin-Elmer LCI-100 integrator. The organic acids were determined as their ethyl esters, by treating the organic phase with ethyl alcohol and a few drops of 96% H_2SO_4, until complete transformation into the ester at room temperature (≈15 h) and analyzing it by GLC in the same conditions adopted for 1-hexyne.

Acknowledgment. The financial support of the Italian Ministry of Education (M.P.I. Rome) is greatly appreciated.

Registry No. $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; $C_6H_5C{\equiv}CH$, 536-74-3; $CH_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3$, 1942-45-6; $CH_3(CH_2)_3C{\equiv}CH$, 693-02-7; $C_6H_5COCOC_6H_5$, 134-81-6; C_6H_5COOH, 65-85-0; $C_6H_5COCH_3$, 98-86-2; $CH_3(CH_2)_2COCO(CH_2)_2CH_3$, 5455-24-3; $CH_3(CH_2)_2COOH$, 107-92-6; $CH_3(CH_2)_2CO(CH_2)_3CH_3$, 589-63-9; $CH_3CH_2CH{=}CHCO(CH_2)_2CH_3$, 762-06-1; $CH_3(CH_2)_3COCH_3$, 591-78-6; HCOOH, 64-18-6; (cetylpyridinium)$_3$PMo(VI)$_{12}$O$_{40}$, 88418-08-0; (cetylpyridinium)$_3$PW(VI)$_{12}$O$_{40}$, 115031-77-1.

A New Hydrogen Source. 3. Chemoselective Reduction with $Et_3NH^+H_2PO_2^-\bullet nH_2O$/Raney Nickel and $RuCl_2(PPh_3)_3$ Reagents

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Triethylammonium hypophosphite hydrate acts as a $NaH_2PO_2{\cdot}H_2O$ modified reagent. Some advantages are noted, including higher product selectivity. Pure aromatic and aliphatic aldehydes are obtained from nitriles by the $Et_3NH^+H_2PO_2^-$/Raney nickel system. The homogeneous catalyst can be used with this reagent. The $Et_3NH^+H_2PO_2^-{\cdot}nH_2O/RuCl_2(PPh_3)_3$ system selectively reduces aromatic and aliphatic ketones to the corresponding alcohols with excellent yields at room temperature.

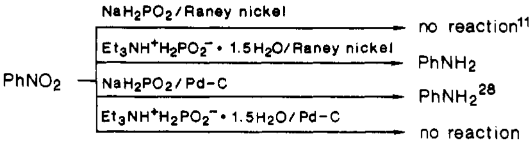
In the hydrogenation of organic compounds with gaseous hydrogen, a few problems require attention, for example, the danger of explosion and the fact that special apparatus which works under pressure is required.[1] Hydrogen in the gaseous phase also presents some problems of storage and transportation;[2-5] therefore, some hydrogen carriers such as metal alloy,[3] magnesium anthracene,[4] and cyclohexane[5] have been proposed.

We have recently investigated some new organic compounds which liberate hydrogen at room temperature and pressure with the assistance of a transition-metal catalyst.[6,7] We have found that they can be successfully used as reducing agents and have some advantages such as operating ease and safety during hydrogenation. A high selectivity in the reduction was observed. For instance, the HCO_2H/Et_3N reagent rapidly liberates hydrogen gas at 20 °C in the presence of $RuCl_2(PPh_3)_3$ and selectively reduces the aldehyde group;[6] in the presence of Pd on carbon, it selectively reduces the nitro group.[7]

Now we have also found that the $Et_3NH^+H_2PO_2^-{\cdot}nH_2O$ reagent rapidly liberates hydrogen in the presence of Raney nickel or $RuCl_2(PPh_3)_3$ at room temperature and selectively reduces nitrile and ketone groups.

Results and Discussion

The $Et_3NH^+H_2PO_2^-{\cdot}nH_2O$ reagent was prepared from equimolar amounts of Et_3N and H_3PO_2 (50%). It is liquid and stable in ambient conditions and soluble in some dry solvents such as THF, dioxane, methanol, ethanol, and DMF. Its activity and selectivity have shown some differences from those of $NaH_2PO_2{\cdot}H_2O$. For example,



Higher product selectivity has also been found (Table I, experiment no. 4, 5). A great advantage is that a homo-

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[1] (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 1–8. (b) Brown, C. A.; Brown, H. C. *J. Org. Chem.* **1966**, *31*, 3989.

[2] Kekley, J. H.; Hagler, R. *Int. J. Hydrogen Energy* **1980**, 35.

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[4] Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 262.

[5] Cacciola, G.; Giodano, N.; Restuccia, G. *Int. J. Hydrogen Energy* **1984**, 411.

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[7] Khai, B. Th.; Arcelli, A. *J. Organomet. Chem.* **1986**, *309*, C63, Part II.

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Table I. Reduction of Nitriles to Aldehydes with Raney Nickel

		products of benzonitrile (PhCN): yield, %				products of aliphatic nitriles (RCH_2CN): yield, %	
expt no.	reagents	PhCN	PhCHO	$PhCH_2OH$	$PhCH_2NH_2$	RCH_2CN	RCH_2CHO
1	hydrazine[a]		87				
2	hydrogen[b]	0–45	20–85	0–41	5–40		20–40
3	NaH_2PO_2[c]		85				20
4	NaH_2PO_2[d]	1–20	65–80	5–15	4–10		
5	$Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$[e]	4	96			2–10	90–98

[a] Reference 9. [b] Reference 10. [c] Reference 11. [d] According to the method in ref 11, the yield and ratio of products are variously found, depending on the temperature and on the % of components of solvents: H_2O/pyridine/AcOH. [e] See Table II (experiments 9–12).

Table II. Reduction by the $Et_3NH^+H_2PO_2^-\bullet 1.5H_2O$/Raney Nickel System at 0 °C

		product[a]		substrate recovered:
expt no.	substrate	compound	yield, %	yield, %
1	nitrobenzene[b]	aniline	100	
2	cyclohexanone oxime[b]	cyclohexanone	79	21
3	1-nitro-1-cyclohexene[b]	cyclohexanone	86	14
4	*p*-chloroacetophenone[b]			100
5	ethyl *trans*-3-(*p*-chlorophenyl)-2-propenoate[b]	ethyl 3-(*p*-chlorophenyl)propanoate	9	91
6	benzaldehyde[b]	benzyl alcohol	15	85
7	2-furonitrile[c]	furfural	97 (91)	*d*
8	2-thiophenecarbonitrile[c]	2-thiophenecarboxaldehyde	100 (91)	
9	benzonitrile	benzaldehyde	96 (91)	4
10	phenylacetonitrile[e]	phenylacetaldehyde	92 (87)	8
11	valeronitrile[e]	valeraldehyde	90 (78)	10
12	5-chlorovaleronitrile[e]	5-chlorovaleraldehyde	98 (90)	2

[a] Determined by GLC. In parentheses are the yields of isolated product. All products are fully confirmed by comparison with authentic samples. [b] Substrates displace to nitriles as in the Experimental Section, part A. [c] The reaction is strongly exothermic; therefore, substrates are added drop by drop and the conversion is completed in 1.5 h. [d] The conversion is 100%, but byproducts are 3%. [e] The yield of aldehyde is improved by adding once more the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$/Raney nickel (see Experimental Section, part A).

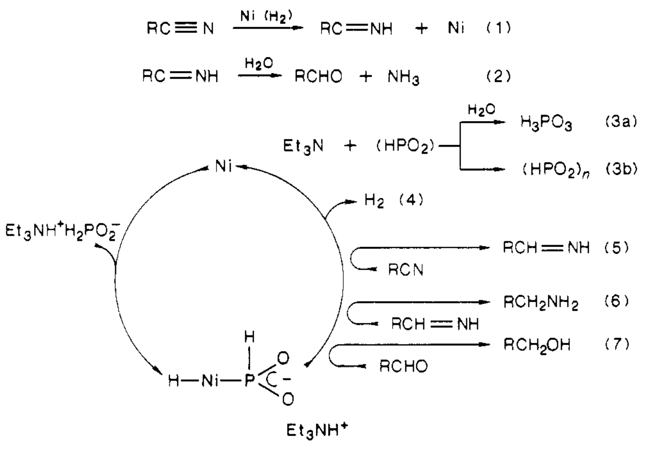
geneous catalyst can be used with this reagent. The $RuCl_2(PPh_3)_3$ complex oxidized $Et_3NH^+H_2PO_2^-\cdot H_2O$ to $Et_3NH^+H_2PO_3^-$ at room temperature and selectively reduced ketone groups, while it had no catalytic activity with NaH_2PO_2. An explanation for this fact is that NaH_2PO_2 probably gives a very strong coordination with ruthenium, similar to our recent report, in which alkyne and salicylaldehyde were seen to be catalytic poisons for $RuCl_2(PPh_3)_3$.[6]

We have found that the quantity of water in the salt of $Et_3NH^+H_2PO_2^-\cdot nH_2O$ has an effect on the catalytic activity: there is good activity when this salt contains from one to two molecules of water (n = 1–2) whereas when there are more than three molecules of water (n > 3), the reaction is erratic. When triethylammonium hypophosphite is dry (n = 0), the reaction is slow, but when one molecule of water is added to this dry salt, both Raney nickel and $RuCl_2(PPh_3)_3$ become more active and the hydrogen gas is rapidly evolved.

A. The $Et_3NH^+H_2PO_2^-\cdot nH_2O$/Raney Nickel System. The $Et_3NH^+H_2PO_2^-\cdot nH_2O$ reagent rapidly liberates hydrogen in the presence of Raney nickel, and it can be used as a good reductive hydrolytic reagent: cyclohexanone oxime and 1-nitro-1-cyclohexene were converted to cyclohexanone without cyclohexylamine; also aromatic and aliphatic nitriles were reduced to the corresponding aldehydes in excellent yields. Byproducts (amines, imines, and alcohols) were not detected (Table II).

The reduction of nitriles directly to aldehydes has been reported by Tolbert and Houston with $SnCl_2\cdot HCl$,[8] by Pietra with hydrazine,[9] by Plieninger and Tinapp[10] with gaseous hydrogen, and by Backeberg[11] with NaH_2PO_2. But the reaction seems to be limited to aromatic nitriles, and byproducts are often present (see Table I). Also, DIBAH seems to be suitable for this reaction, but with organoaluminum compounds there are some operating problems; also, being a strong reducing agent, it must be used with caution to prevent overreduction and reduction of other functional groups present.[12-14]

Scheme I



In the conversion of nitriles to aldehydes, we have found that there is competition between hydrogenation and hydrolysis. In our system, the $Et_3NH^+H_2PO_2^-\cdot nH_2O$ contains about $1{-}2H_2O$, and the reaction is carried out at 0 °C;

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(8) Tolbert, T. L.; Houston, B. *J. Org. Chem.* **1963**, *28*, 695.

(9) Pietra, S.; Trinchera, C. *Gazz. Chim. Ital.* **1955**, *85*, 1705.

(10) (a) Plieninger, H.; Werst, G., *Chem. Ber.* **1955**, *88*, 1956. (b) Tinapp, P. *Ibid.* **1969**, *102*, 2770.

(11) Backeberg, O. G.; Staskun, B. *J. Chem. Soc.* **1962**, 3961.

(12) Winterfeldt, E. *Synthesis* **1975**, 617.

(13) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; J. Wiley and Sons, Inc.: New York, 1967; Vol. 1, pp 260–262.

(14) Miller, A. E. G.; Biss, J. W.; Schwartzman, L. H. *J. Org. Chem.* **1959**, *24*, 627.

Table III. Reduction of Ketones to Alcohols by the $Et_3NH^+H_2PO_2^-\bullet 1.5H_2O/RuCl_2(PPh_3)_3$ System at Room Temperature for 24 h

expt no.	ketone	product[a] compound	product[a] yield, %	ketone recovered: yield, %
1	acetophenone[b]	1-phenylethanol	81	19
2	propiophenone[b]	1-phenylpropanol	91 (81)	9
3	*p*-methylacetophenone[b]	1-(*p*-tolyl)ethanol	73	17
4	*p*-nitroacetophenone[b]	1-(*p*-nitrophenyl)ethanol	100 (94)	0
5	*p*-chloroacetophenone[b]	1-(*p*-chlorophenyl)ethanol	95 (89)	5
6	nitrobenzene +	nitrobenzene +	100	
	acetophenone	1-phenylethanol	65	35
7	cyclohexanone	cyclohexanol	99 (94)	1
8	4-*tert*-butylcyclohexanone[b]	4-*tert*-butylcyclohexanol (cis/trans 47/49)	96	4
9	4-*tert*-butylcyclohexanone[c]	4-*tert*-butylcyclohexanol (cis/trans 64/33)	97	3
10	2-methylcyclohexanone[b]	2-methylcyclohexanol (cis/trans 93/0.7)	94	6
11	camphor[b]	borneol	17	83
12	2-octanone[b]	2-octanol	92 (90)	8
13	ethyl acetoacetate	ethyl 3-hydroxybutyrate	96 (90)	4
14	6-methyl-5-hepten-2-one	6-methyl-5-hepten-2-ol	86 (80)	14

[a] Determined by GLC. In parentheses are the yields of isolated products. All products are fully confirmed by comparison with authentic samples. [b] The yield of alcohol is improved by adding once more the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ reagent. [c] The dry $Et_3NH^+H_2PO_2^-$ reagent is used and the yield is determined after three successive additions of reagent.

therefore, Ni slowly oxidized H_3PO_2. In the Backeberg system, the reaction is at room temperature and H_2O is used as a solvent, and Ni rapidly oxidizes H_3PO_2 and gives abundant "Ni–H"; therefore, hydrogenation is a predominant reaction. In contrast, in our system, hydrolysis is predominant (Scheme I, eq 2).

Similarly to previous reports of other authors,[11,15] we have also found that catalytic activity plays an important part in this reaction. Benzonitrile with freshly prepared Raney nickel W-2 gave byproduct benzylamine, which was no longer found after Raney nickel had been stored under water for about 1 month. Good results were also obtained with Raney nickel (ready for use from Fluka), but a larger quantity was required. In order to operate with ease, in this work we have used commercial Raney nickel from Fluka. The $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$/Raney nickel (Fluka) is almost ineffective for aromatic and aliphatic aldehydes. At 23 °C, overreduction of aldehydes can occur and a small quantity of alcohols was found, but at 0 °C, even when an excess of reagent or a long reaction time was used, alcohols were not detected. The displacement of benzonitrile by benzaldehyde after 6 h gave 15% of benzyl alcohol and left the remaining aldehyde unchanged (Table II, experiment no. 6). This finding is contrary to previous reports[10,15,16] of hydrogenation with hydrogen gas: Adkins[16] has reported that the hydrogenation rate of aldehydes and ketones was increased in the presence of Et_3N at room temperature; Plieninger[10] has proposed using semicarbazide to protect aldehydes in nitrile hydrogenation; and recently D. P. Curran[15] has reported that the reduction of *p*-anisaldoxime produced a mixture of amines and alcohols with no aldehyde being present.

In a recent report of ours,[17] benzylamine was converted to dibenzylamine (99%), in a sealed tube, whereas in an open vessel it gave 73% of *N*-benzylidenebenzylamine. This can be explained as being due to the desorption of hydrogen, which is the predominant reaction in an open vessel. The fact that the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$/Raney nickel system is almost ineffective for aldehydes suggests once again that the desorption of hydrogen (Scheme I, eq 4) is more rapid than the hydrogenation (eq 6, 7), in contrast to the reduction under hydrogen gas where hydrogenation is predominant. We propose, moreover, that chemoselective reduction is due to a partially deactivated catalyst by rearrangement of the surface structure of the catalyst;[18] the competition between the hydrogenation and desorption of hydrogen on the catalyst can also play an important role in chemoselective reduction. The above evidence leads us to favor a mechanistic hypothesis for the reductive–hydrolytic reaction with Raney nickel which closely resembles that proposed previously for palladium with H_3PO_2.[20]

In conclusion, the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$/Raney nickel system in THF/MeOH acts as a modification of the NaH_2PO_2/Raney nickel in $H_2O/AcOH$/pyridine system, but byproducts are completely avoided, pure aromatic and aliphatic aldehydes are obtained, and this system is easy to work with.

B. The $Et_3NH^+H_2PO_2^-\cdot nH_2O/RuCl_2(PPh_3)_3$ System. The $RuCl_2(PPh_3)_3$ complex has been reported as an effective catalyst for the reduction of ketone groups to alcohols at different temperatures depending on the hydrogen source: at 180 °C with alcohol,[21] at 150 °C with gaseous hydrogen,[22] and at 125 °C with formic acid.[23]

In a recent study of ours,[6] we reported that $RuCl_2(PPh_3)_3$ catalyzed the reduction of acetophenone at 75 °C with HCO_2H/Et_3N as the hydrogen source. Now we have found that this complex, in the presence of the $Et_3NH^+H_2PO_2^-\cdot nH_2O$ liquid reagent, affords a highly active catalyst and reduces ketones even at 20 °C. To the best of our knowledge, this is the first case in which this complex actively catalyzes the ketone reduction in very high yield at room temperature and pressure.

In fact, in the presence of a small amount of $RuCl_2(PPh_3)_3$, the $Et_3NH^+H_2PO_2\cdot nH_2O$ reagent immediately

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(15) Curran, D. P.; Brill, J. F.; Rakiewicz, D. M. *Ibid.* **1984**, *49*, 1654.

(16) Levering, D. R.; Lieber, E. *J. Am. Chem. Soc.* **1949**, *71*, 1515.

(17) Khai, B. Th.; Concilio, C.; Porzi, G. *J. Organomet. Chem.* **1981**, *208*, 249.

(18) The partially deactivated catalyst. (a) Raney nickel with acetic acid: Sraga, J.; Hrnciar, P. *Synthesis* **1977**, 282. (b) Raney nickel with acetone: Reference 15. (c) Pd–C with Et_3N: Dobson, N. A.; Eglinton, G.; Krishnamurti, M.; Raphael, R. A.; Willis, R. G. *Tetrahedron* **1961**, *16*, 16. (d) Pd–C with mercury: Johnstone, R. A. W.; Wilby, A. H. *Tetrahedron* **1981**, *37*, 3667. (e) Lindlar catalyst: McEwen, A. B.; Guttieri, M. J.; Maier, W. F.; Laine, R. M.; Shvo, Y. *J. Org. Chem.* **1983**, *48*, 4436.

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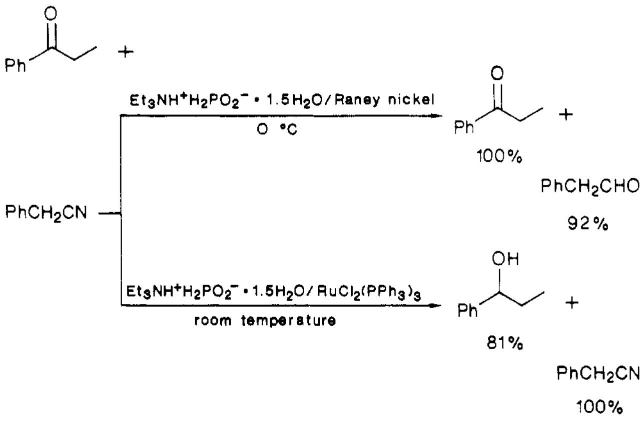
(20) Johnstone, R. A. W.; Wilby, A. H. *Chem. Rev.* **1985**, *85*, 129.

(21) Sasson, Y.; Albin, P.; Blum, J. *Tetrahedron Lett.* **1974**, 833.

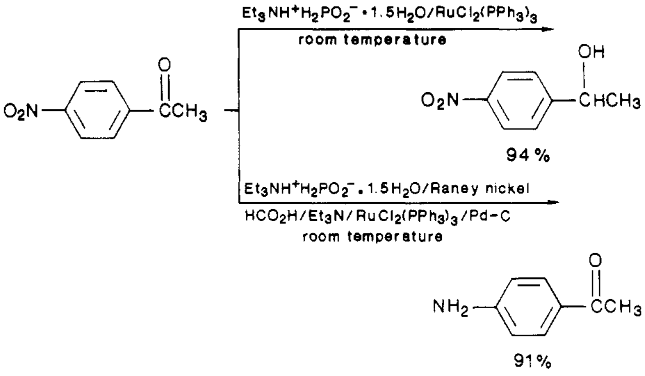
(22) Delgado, R. A. S.; De Ochoa, O. L. *J. Organomet. Chem.* **1980**, *202*, 427.

(23) Watanabe, Y.; Ohta, T.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2441.

Scheme II



Scheme III



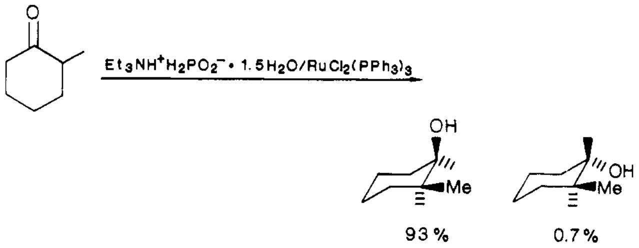
releases hydrogen gas and reduces the aldehyde[24] and ketones at room temperature. The results are summarized in Table III. Different activity and selectivity of the $RuCl_2(PPh_3)_3$ catalyst between two reagents, $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ and dry $Et_3NH^+H_2PO_2^-$, were noted. $RuCl_2(PPh_3)_3$ oxidizes H_3PO_2 to (HPO_2) and probably could be converted to the $RuHCl(PPh_3)_3$ complex as key intermediate, similarly to previous reports by G. Winkinson[25] and P. E. Garrou.[26] In the absence of water, (HPO_2) gives polymer $(HPO_2)_n$, which absorbs the catalyst; in this case, the catalyst loses partial activity. This is similar to the finding of our other work in which we have found that $RuCl_2(PPh_3)_3$ supported on diphenylphosphinated polystyrene resins is less active than $RuCl_2(PPh_3)_3$ itself.[27] We have found that, in this case, the catalyst becomes sluggish but offers a highly steric selectivity: 4-*tert*-butylcyclohexanones gives a greater quantity of the thermodynamically less stable alcohol (cis/trans ratio 66/34) with a dry reagent, in comparison with the ratio 49/51 with a hydrated reagent (Table III, experiments 8, 9).

As reported in recent papers,[6,7] our reagents are exceptionally suitable for selective reduction, and in this case we have also found that the $Et_3NH^+H_2PO_2^-\cdot nH_2O$/$RuCl_2(PPh_3)_3$ system preferentially reduces ketones in the presence of other reducible functional groups.

Table IV. Reduction of Ketones to Alcohols by the $Et_3NH^+H_2PO_2^-\bullet 1.5H_2O/RuCl_2(PPh_3)_3$ System at Room Temperature for 2 h

expt no.	ketone	yield of alcohol, %
1	acetophenone	43
2	*p*-methylacetophenone	40
3	*p*-chloroacetophenone	75
4	*p*-nitroacetophenone	100
5	cyclohexanone	75
6	4-*tert*-butylcyclohexanone	61
7	2-methylcyclohexanone	42
8	camphor	7

Scheme IV



Besides the partially deactivated catalyst and the competition between the hydrogenation and desorption of hydrogen on catalyst, we note a third factor: the nature of the transition metal also plays a determining role in chemoselective reduction, and in fact, we have found proof of opposite chemoselective reduction with the $Et_3NH^+H_2PO_2^-\cdot nH_2O$ hydrogen source. When Raney nickel is used, only phenylacetonitrile is reduced to phenylacetaldehyde, but when $RuCl_2(PPh_3)_3$ is used, only propiophenone is reduced to 1-phenylpropanol, as shown in Scheme II. Scheme III shows the chemoselective reduction of the ketone and nitro groups.

We have found that, in our system, conversion is rapid and complete or slow and incomplete, but byproducts such as hydrocarbon (Clemmensen reduction) or pinacol (dimerization) are not detected. Disadvantageous incomplete conversion can be improved by successive addition of the reagent (see Table III). As recently reported, we have found[6,17] that the steric effects play an important role in the rate of reaction catalyzed by $RuCl_2(PPh_3)_3$. The greater rate of reduction of cyclohexanone in comparison with 2-methylcyclohexanone and camphor (see Table IV) can be ascribed to this factor, and in this case the $RuCl_2(PPh_3)_3$ catalyst has a great advantage: stereoselective reduction, 2-methylcyclohexanone giving 93% of *cis*-2-methylcyclohexanol (Scheme IV).

In contrast with the reduction of aldehydes by the $HCO_2H/Et_3N/RuCl_2(PPh_3)_3$ system,[6] the substituent effect on the benzene ring seems to influence the reduction rate of acetophenone as shown in Table IV. The transfer of hydride from the ruthenium complex to the electron-deficient center of the ketone group probably also plays an important role in this reaction.

C. The $Et_3NH^+H_2PO_2^-\cdot nH_2O$/Pd-C System. In contrast to NaH_2PO_2,[28-30] Pd-C almost lost its catalytic activity with $Et_3NH^+H_2PO_2^-\cdot nH_2O$. Nitrobenzene, chlorobenzene, acetophenone, and methylcinnamate remained unchanged after 1 day; 1-bromo-2-nitrobenzene gave a

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[24] Benzaldehyde was rapidly reduced to benzyl alcohol (95%), in 2 h in the case in which ketone was displaced by benzaldehyde as in the Experimental Section, part B.

[25] Hallman, P. S.; Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1967**, 305.

[26] (a) Jung, Ch. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042. (b) Jung, Ch. W.; Garrou, P. E. *Ibid.* **1982**, *1*, 658.

[27] We have tried the methylation of primary amines (ref 19) and the decomposition of formic acid (ref 6); $RuCl_2(PPh_3)_3$ supported on diphenylphosphinated polystyrene resins is more stable (longer lifetime) but less active than $RuCl_2(PPh_3)_3$ itself (unpublished results).

[28] Entwistle, I. D.; Jackson, A. E.; Johnstone, R. A. W.; Telford, R. P. *J. Chem. Soc., Perkin Trans. 1* **1977**, 443.

[29] Sala, R.; Doria, G.; Passarotti, C. *Tetrahedron Lett.* **1984**, *25*, 4565.

[30] Boyer, S. K.; Bach, J.; McKenna, J.; Jagdmann, E., Jr. *J. Org. Chem.* **1985**, *50*, 3408.

mixture of products, but no hydrogen evolution was detected.

Experimental Section

General. W-2 Raney nickel was prepared according to ref 31. Raney nickel (ready for use in water) and hypophosphorous acid (50% wt in water) were purchased from Fluka. THF was distilled from sodium benzophenone ketyl. Other reagents were obtained commercially and used without further purification. Infrared (IR) spectra were measured on a Perkin-Elmer PE 682 spectrophotometer; ^1H NMR spectra were measured in $CDCl_3$ at 90 MHz on a Varian EM 390 instrument; chemical shifts are reported in δ units using Me_4Si as internal standard. Capillary gas chromatography (GLC) was performed on Carlo Erba HRGC 5300 Mega series apparatus using the following columns: OV1 (0.1-μm diameter, 15-m length); Carbowax 20M (0.4 μm, 20 m); and SE 52 (0.1 μm, 25 m).

The $Et_3NH^+H_2PO_2^-\cdot nH_2O$ Reagent. H_3PO_2 (54.5 mL, 66 g (50% wt in water from Fluka) was placed in a flask immersed in an ice bath; then 69.7 mL (50.6 g) of Et_3N was slowly added and the mixture shaken after each addition until a homogeneous solution was obtained, whereupon water was removed by distillation in two ways: (a) At 40–50 °C under 15 mmHg after 30 min, about 17 g of H_2O was removed, leaving 96.3 g of liquid $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ in the flask; and after 1 h, 21 g of water was removed and 91 g of $Et_3NH^+H_2PO_2^-\cdot H_2O$ remained. (b) At 65 °C under 0.2 mmHg for 3 h, not only water but also Et_3N was removed (about 42 g), leaving 69 g of dry $Et_3NH^+H_2PO_2^-$ reagent.

A. Reduction of Nitriles to Aldehydes by the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$/Raney Nickel System. Moist Raney nickel (5 g) (Fluka) was placed into a flask containing 10 mL of THF and 5 mL of EtOH, 95%, at 0 °C, then 4 mL of the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ reagent was added all at once, and immediately an evolution of hydrogen was observed. The reaction was exothermic, and the temperature rose to 8–10 °C. When the temperature began to fall, 0.01 mol of nitrile was added, and the solution was kept at 2–3 °C for 2 h. In the cases in which conversion was not complete (Table II, experiments 10–12), the solution was cooled to 0 °C, 1 g of Raney nickel was added, and then 1 mL of $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ was added. The addition of reagent can be repeated until conversion is complete (determined by GLC and compared with authentic samples). The solution was then stirred at 2–3 °C for 4–5 h. Finally, the products were extracted three times with 20 mL of ether, washed three times with 25 mL of water, and dried over $MgSO_4$. After solvent evaporation, the aldehydes were found from IR and NMR spectra to be sufficiently pure, and after the products were chromatographed over a short column of silica gel with ether/hexane as eluant, their boiling points were in agreement with those found in the literature (Table II).

B. Reduction of Ketones to Alcohols by the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O/RuCl_2(PPh_3)_3$ System. The ketone (0.006 mol) and 4 mL of the $Et_3NH^+H_2PO_2^-\cdot 1.5H_2O$ were mixed in a flask under a nitrogen atmosphere at room temperature and stirred until a homogeneous solution was obtained. Then 6×10^{-5} mol of $RuCl_2(PPh_3)_3$ was added to the solution, and immediately hydrogen was evolved (after 2 h, if 70% conversion was not achieved, determined by GLC, another 0.5 mL of $Et_3N^+H_2PO_2^-\cdot 1.5H_2O$ and 0.020 g of $RuCl_2(PPh_3)_3$ were added). The solution was stirred overnight, then 20 mL of water was added, and the products were extracted three times with 20 mL of ether or CH_2Cl_2. Finally the solution was washed with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was analyzed by IR and ^1H NMR spectra and GLC by comparison with authentic samples (Table III).

Registry No. $Et_3NH^+H_2PO_2^-$, 117872-98-7; $RuCl_2(PPh_3)_3$, 15529-49-4; Raney nickel, 7440-02-0; nitrobenzene, 98-95-3; cyclohexanone oxime, 100-64-1; 1-nitro-1-cyclohexene, 2562-37-0; *p*-chloroacetophenone, 99-91-2; ethyl *trans*-3-(*p*-chlorophenyl)-2-propenoate, 24393-52-0; benzaldehyde, 100-52-7; 2-furonitrile, 617-90-3; 2-thiophenecarbonitrile, 1003-31-2; benzonitrile, 100-47-0; phenylacetonitrile, 140-29-4; valeronitrile, 110-59-8; 5-chlorovaleronitrile, 6280-87-1; aniline, 62-53-3; cyclohexanone, 108-94-1; ethyl 3-(*p*-chlorophenyl)propanoate, 7116-36-1; benzyl alcohol, 100-51-6; furfural, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3; phenylacetaldehyde, 122-78-1; valeraldehyde, 110-62-3; 5-chlorovaleraldehyde, 20074-80-0; acetophenone, 98-86-2; propiophenone, 93-55-0; *p*-methylacetophenone, 122-00-9; *p*-nitroacetophenone, 100-19-6; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methylcyclohexanone, 583-60-8; camphor, 76-22-2; 2-octanone, 111-13-7; ethyl acetoacetate, 141-97-9; 6-methyl-5-hepten-2-one, 110-93-0; 1-phenylethanol, 98-85-1; 1-phenylpropanol, 93-54-9; 1-(*p*-tolyl)ethanol, 536-50-5; 1-(*p*-nitrophenyl)ethanol, 6531-13-1; 1-(*p*-chlorophenyl)ethanol, 3391-10-4; cyclohexanol, 108-93-0; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *cis*-2-methylcyclohexanol, 7443-70-1; borneol, 507-70-0; 2-octanol, 123-96-6; ethyl 3-hydroxybutyrate, 5405-41-4; 6-methyl-5-hepten-2-ol, 1569-60-4.

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(31) Mozingo, R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 181.

Design of Concerted Multicenter Reactions

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The transition state of a one-step "allowed" reaction is stabilized by charge alternation at the four union sites. In order to promote such bizwitterionic character, the "observer" σ-bonds must be weak and, hence, polarizable. It is argued that the fine balance between a one-step "allowed" and a two-step mechanism involving diradical intermediates is determined by the σ-bonds of reacting polyenes, and specific illustrations, using data drawn from the literature, are presented. The message for the experimentalist is as follows: To enforce a concerted "allowed" reaction, make the "observer" bonds weak by replacing first row atoms by their heavier congeners, e.g., C by Si, etc.

The pioneer work of Hueckel[1] and the pivotal contribution of Heilbronner regarding the Hueckel–Moebius distinction[2] provide an answer to the following question: Given a cyclic array of *m* orbitals containing *n* electrons, what is the dependence of the stabilization energy on the number of orbital phase changes, odd versus even, one encounters in travelling around the ring? The answer is

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[1] (a) Hueckel, E. *Z. Physik.* **1930**, *60*, 423. (b) Heilbronner, E.; Bock, H. *Das HMO-Modell und Seine Anwendung*; Verlag Chemie, Gmbh: Weinheim, 1968.

[2] Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923.

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