flushing with O_2 for 1 min, a small, constant overpressure of O_2 was kept over the magnetically stirred reaction mixture.[31] A few crystals of $NO^+BF_4^-$ were rapidly added, and stirring was continued for the appropriate reaction period at room temperature; in many cases colorless solutions were obtained at the end of reaction. The reaction mixture was poured onto aqueous $Na_2S_2O_3/CHCl_3$ and the aqueous layer washed with $CHCl_3$, and the combined organic layers were washed with water, aqueous $NaHCO_3$, and water and dried ($MgSO_4$). After evaporation and passage through a short column the yield was determined by GLC or workup continued by chromatography (and/or recrystallization in some cases) as described in the tables.

Special Procedures. A. Relative Rates. Values of k_{rel} were determined by allowing NH_4I to be competed for by a tenfold excess of the aromatic compounds (ratio 1:1 or 10:1) in any of the systems A-D in Table I. The relative rates of 27 different pairs were determined.

B. Isotope Effects. Values of k_H/k_D were determined by allowing 1.00 mmol each of, e.g., toluene and toluene-d_8 to compete for 0.20 mmol of NH_4I in 17 mL of CF_3COOH/1 mL of $(CF_3CO)_2O$ (in the naphthalene case 2 mL of CH_2Cl_2 was added) under O_2 at 25 °C for 2-3 h. After workup the values of k_H/k_D were calculated either from the mass spectrometric data or directly from the gas chromatograms obtained on column A.

C. Catalytic Efficiency. The catalytic efficiency of $NO^+BF_4^-$ was determined by treating 1.5 mmol of *p*-xylene and 1.0 mmol of NH_4I in 10 mL of CF_3COOH, 0.5 mL of $(CF_3CO)_2O$, and 1.0 mL of CH_2Cl_2 under O_2 for 5 h with 0.01-0.09 mmol of $NO^+BF_4^-$. Results [mmol of $NO^+BF_4^-$ (% yield)]: 0.09 (95); 0.068 (98); 0.048 (97); 0.025 (90); 0.019 (72); 0.011 (35).

D. Sources of "I". The yields of iodomesitylene from essentially the procedure as in C albeit with 0.08-0.10 mmol of $NO^+BF_4^-$ and a 1.5-h reaction period were in the 95-100% range for NH_4I, NaI, KI, $(n\text{-}C_4H_9)_4NI$, and I_2.

E. Synthesis of Iodomesitylene. Mesitylene (0.11 mol) and NH_4I (0.10 mol) were treated with $NO^+BF_4^-$ (0.001 mol) in 150 mL of CH_3COOH, 15 mL of CF_3COOH, and 10 mL of $(CH_3CO)_2O$ under O_2 at 25 °C for 48 h. At the end of reaction the solution turned colorless, and after workup as described above iodomesitylene (0.095 mol, 95%, recrystallized from a small volume of ethanol) was obtained.

F. Synthesis of 1-Iodo-4-methoxynaphthalene. A mixture of 1-methoxynaphthalene (8.2 mmol), NH_4I (7.5 mmol), CH_3COOH (30 mL), CF_3COOH (4 mL), and $(CH_3CO)_2O$ (2 mL) was stirred under O_2, and $NOBF_4$ (0.15 mmol) was added. After 16 h, the mixture was worked up, yielding 1-iodo-4-methoxynaphthalene (6.4 mmol, 85%): mp (ethanol) 54-56 °C (lit.[32a] mp 54-55 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 3), 6.60 (d, 1), 7.55 (m, 2), 7.95 (d, 1), 8.03 (d, 1), 8.23 (d, 1); mass spectrum, *m/e* (relative intensity) 284 (45), 269 (24), 241 (26), 157 (10), 142 (20), 128 (10), 127 (20), 126 (22), 114 (100).

Acknowledgment. I thank Professor Lennart Eberson for stimulating discussions and the Swedish Natural Science Research Council for financial support.

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(31) When O_2 was replaced by air (furnished via a drying tube) aryl iodides generally were formed, albeit at lower rates, from substrates more reactive than toluene.

(32) (a) Baddar, G. F.; El-Assal, L. S.; Baghos, V. B. *J. Chem. Soc.* **1958**, 986. (b) Bergmann, E. D.; Shahak, I. *Ibid.* **1959**, 1418.

Selective Oxidation of Alcohols by a H_2O_2-$RuCl_3$ System under Phase-Transfer Conditions

Gabriela Barak, Jihad Dakka, and Yoel Sasson*

Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

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The selective oxidation of primary aliphatic alcohols to carboxylic acids (60-70% selectivity), secondary alcohols to ketones (100% selectivity), and primary benzylic alcohols to aldehydes (95-100% selectivity) or carboxylic acids as well as the selective oxidation of allylic alcohol to ketones (80% selectivity) was performed in a H_2O_2-$RuCl_3 \cdot 3H_2O$ phase transfer catalyst (PTC) system at a high substrate:$RuCl_3$ (625:1) ratio. It has also been found that the PTC not only has a role in the extraction of $RuCl_3$ and H_2O_2 in the organic phase but also protects the metallic catalyst against reduction. Other metallic catalysts as $PdCl_2$, $RhCl_3 \cdot 3H_2O$, $MnCl_2 \cdot 4H_2O$, and $CoCl \cdot 6H_2O$ show poor conversion and selectivity.

The metal-promoted hydrogen peroxide oxidation of various alcohols to aldehydes, ketones, or carboxylic acids is usually performed in the presence of a polar solvent in order to overcome the solubility problems of both the metal salt catalyst and hydrogen peroxide.

Solvents like acetone,[1,2] methanol,[3] and even water[4] (for water-soluble glycols) are cited in literature, but the use of those is quite limited. For example, under the reaction conditions, acetone can form very explosive dimeric or trimeric peroxides[5] and methanol can be oxidized by itself.

It has recently been found that phase-transfer catalysts (PTC) can effectively replace the polar solvents in these reactions, when catalyzed by molybdate or tungstate anions.[6-9] However, these procedures are of limited preparative value since they use high catalyst:substrate ratios (1:10 to 1:40) and sometimes high hydrogen peroxide concentrations[6] (up to 70%).

We now report that aqueous 30% hydrogen peroxide solution in conjunction with catalytic amounts of $RuCl_3$ (catalyst:substrate ratio 1:625) under PTC conditions

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(1) Jpn. Pat. Appl. 79-9639; *Chem. Abstr.* **1981**, *94*, 467836.

(2) Gore, E. S. *Platinum Met. Rev.* **1983**, *27*, 111.

(3) Sheldon, R. A. *Bull. Soc. Chim. Belg.* **1985**, *94*, 651.

(4) Venturello, C.; Ricci, M. *J. Org. Chem.* **1986**, *51*, 1599.

(5) Bretherick, L. *Handbook of Reactive Chemical Hazards*, 2nd ed.; Butterworths: London, 1979.

(6) Bortolini, O.; Conte, V.; di Furia, F.; Modena, G. *J. Org. Chem.* **1986**, *51*, 2661.

(7) Bortolini, O.; Conte, V.; di Furia, F.; Modena, G. *Nouv. J. Chim.* **1985**, *9*, 147.

(8) Trost, B. M.; Masuyama, Y. *Isr. J. Chem.* **1984**, *24*, 134.

(9) Trost, B. M. Masuyama, Y. *Tetrahedron Lett.* **1984**, *25*, 173.

0022-3263/88/1953-3553$01.50/0 © 1988 American Chemical Society

Table I. Oxidation of Alcohols by a H_2O_2–$RuCl_3$ System under PTC Conditions

alcohol	conv, %	main product	selectivity, %
cyclohexanol[b]	90	cyclohexanone	100
2-octanol[b]	82	2-octanone	100
sec-phenethyl alcohol[b]	90	acetophenone	100
benzyl alcohol[a]	91	benzaldehyde	95
benzyl alcohol[b]	95	benzoic acid	100
p-methylbenzyl alcohol[a]	86	*p*-methylbenzaldehyde	100
p-nitrobenzyl-alcohol[a]	80	*p*-nitrobenzaldehyde	100
p-bromobenzyl alcohol[a]	45	*p*-bromobenzaldehyde	100
1-decanol[c]	87	1-decanoic acid	66
1-octanol[c]	85	1-octanoic acid	68
1-heptanol[c]	89	1-heptanoic acid	73
1-hexanol[c]	85	1-butanoic acid	67

[a,b] Reaction conditions: $T = 80$ °C, time (a) 45 min, (b) 90 min; 48 mmol of alcohol, 10 mL of CH_2Cl_2, 0.077 mmol of $RuCl_3{\cdot}3H_2O$, 1 mmol of didecyldimethylammonium bromide (DDAB); H_2O_2, 30%, 130 mmol (15 mL), (a) H_2O_2, 260 mmol (30 mL). [c] For all the primary aliphatic alcohols, 5–10% aldehyde and 10–15% ester were obtained. GLC analysis.

provides a synthetically useful procedure for the oxidation of primary aliphatic alcohols to carboxylic acids, of secondary alcohols to ketones, and of primary benzylic alcohols to aldehydes or carboxylic acids as shown in Scheme I. The selective oxidation of an aliphatic allylic alcohol to an unsaturated ketone has also been performed as shown in Scheme II. We have investigated the effects of various phase-transfer catalysts and some other metal salts on these reactions.

Scheme I

$$RCH_2OH + H_2O_2 \xrightarrow[PTC]{RuCl_3} RCHO + 2H_2O \qquad (1)$$

$$RCHO + H_2O_2 \rightarrow RCOOH + H_2O \qquad (2)$$

$$R_2CHOH + H_2O_2 \xrightarrow[PTC]{RuCl_3} R_2C{=}O + 2H_2O \qquad (3)$$

Scheme II

$$RCHOHCH{=}CH_2 + H_2O_2 \xrightarrow[PTC]{RuCl_3} ROCCH{=}CH_2 + 2H_2O \qquad (4)$$

Results and Discussion

The results for the 30% hydrogen peroxide, $RuCl_3$-catalyzed oxidation of various alcohols under phase-transfer (PT) conditions (didecyldimethylammonium bromide, DDAB, as catalyst) at 80 °C of a variety of alcohols are summarized in Table I.

Significant yields and selectivities were obtained for primary benzylic and secondary aliphatic alcohols, while primary aliphatic alcohols showed lower selectivity.

An interesting observation is that in spite of the fact that reaction 2 is spontaneous at 80 °C we succeeded in obtaining benzaldehyde from benzyl alcohol with high selectivity (95%), provided that the H_2O_2:substrate ratio is not higher than 2.7.

When the oxidation of each of these alcohols was attempted in the absence of the quaternary ammonium phase-transfer catalyst, an immediate precipitation of the reduced metal (Ru^0) was observed. No reduction of the metal was detected at all in the presence of DDAB, suggesting that the role of the PTC is not merely to extract the $RuCl_3$ and hydrogen peroxide into the organic phase but also to protect the metallic catalyst against reduction, apparently by complex formation. Only benzyl alcohol was reactive even in the absence of the phase-transfer catalyst; however, the reaction rate was three times slower (only 30% benzaldehyde was found after 45 min using 120 mmol H_2O_2).

Table II. H_2O_2 Oxidation of Benzyl Alcohol in the Presence of Different Metallic Catalysts under PTC Conditions[a]

catalyst	conv, %	main product	selectivity, %	main byproduct
$RhCl_3{\cdot}3H_2O$	50	benzaldehyde	60	benzoic acid
$PdCl_2$	52	benzaldehyde	60	benzoic acid
$CoCl_2{\cdot}6H_2O$	20	benzaldehyde	70	benzoic acid
$MnCl_2{\cdot}4H_2O$	18	benzaldehyde	72	benzoic acid

[a] Reaction conditions: same as in Table I except reaction time was 24 h. In all the cases some benzyl enzoate was formed.

The large excess amount of hydrogen peroxide required (three or six times the stoichiometric amount) is a result of its simultaneous decomposition in the presence of the $RuCl_3$·catalyst (eq 4). We confirmed that the oxygen released in reaction 5 has no role in the oxidation of the alcohol by performing a reaction under similar conditions but using oxygen gas as oxidant. No reaction occurs.

$$2H_2O_2 \xrightarrow{RuCl_3} 2H_2O + O_2 \qquad (5)$$

In order to minimize the decomposition effect, we examined other metallic catalysts such as $RhCl_3{\cdot}3H_2O$, $PdCl_2$, $CoCl_2{\cdot}6H_2O$, and $MnCl_2{\cdot}4H_2O$, for the oxidation of benzylic alcohol. None of these salts catalyzed the decomposition (eq 4), but the oxidation reactions (eq 1–3) were much slower and the conversion and the selectivity were lower as presented in Table II.

The size of the cation of the PTC is known to affect the extraction of both H_2O_2[10] and metallic salts.[10] We had examined different catalysts, namely, Aliquat 336, tetrabutylammonium bromide, and tetrapropylammonium bromide (TPAB). It was found that all these catalysts showed activity similar to that of the lipophilic DDAB. We conclude that the extraction is not a critical step in the overall mechanism of the catalytic process.

On the basis of our previous finding that aliphatic olefins are not oxidized by the H_2O_2–$RuCl_3$–PTC[11] system, we tried to oxidize a secondary alcohol in the presence of an olefin under the above conditions. Our model was 1-octen-3-ol, and we found that for a conversion of 76% the selectivity for 1-octen-3-one was 80%. Since the system $RuCl_3$–DDAB is not active in oxidation of olefins, we believe that ruthenium tetraoxide, which is known to react with olefins, is not formed in this catalytic cycle. The active intermediates are therefore probably oxo ruthenium complexes of lower oxidation state.

Experimental Section

Materials. All chemicals were standard laboratory chemicals from various commercial companies (Aldrich, Merck, Fluka, and Abic). All the chemicals were of the highest purity available and used with no further purification. The only exception was the DDAB, which came as a 50% toluene solution and was used as such.

Oxidation Procedure for Benzyl Alcohol. The oxidation was performed in a three-neck flask equipped with a condenser, a magnetic stirrer, and a heating bath.

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(10) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, 1983.

(11) Unpublished results.

The reaction vessel was charged with 5 mL (48 mmol) of benzyl alcohol, 10 mL of $(CH_2)_2Cl_2$, 0.02 g (0.077 mmol) of $RuCl_3\cdot 3H_2O$, and 1 mL (1 mmol) of DDAB, 50% in toluene. The H_2O_2, 30% (15 mL), was fed into the reaction mixture by a syringe pump at a constant feed rate of 0.3 mL/min.

When the isolation of pure products was wanted, the organic phase was separated, solvent evaporated, and the residue chromatographed on a silica gel column by gradient elution, beginning with CH_2Cl_2 up to CH_2Cl_2:MeOH, 80:20%.

The procedures for all the other cited substrates are exactly the same as for benzyl alcohol.

Analysis. The progress of the reactions was checked by GLC analysis. When the product was an acid, the sample was first methylated by diazomethane. The column was OV-101 15% on Chromosorb 100/120 WAW for primary aliphatic and benzylic alcohols at a temperature of 100 °C (3 min), 25 °C/min, 250 °C (5 min) and OV 210 10% on Chromosorb 80/100 WHP for secondary alcohols at a temperature of 60 °C (5 min), 25 °C/min, 250 °C (5 min). The identification of the products was done by comparing with a standard and also by CGMS analysis.

Acknowledgment. We are grateful to Abic Ltd. Ramal-Gan for the donation of DDAB.

Registry No. $RuCl_3$, 10049-08-8; $PdCl_2$, 7647-10-1; $CoCl_2$, 7646-79-9; $MnCl_2$, 7773-01-5; didecyldimethylammonium bromide, 19959-22-9; cyclohexanol, 108-93-0; 2-octanol, 123-96-6; *sec*-phenethyl alcohol, 98-85-1; benzyl alcohol, 100-51-6; *p*-methylbenzyl alcohol, 589-18-4; *p*-nitrobenzyl alcohol, 619-73-8; *p*-bromobenzyl alcohol, 873-75-6; 1-decanol, 112-30-1; 1-octanol, 111-87-5; 1-heptanol, 111-70-6; 1-hexanol, 111-27-3; cyclohexanone, 108-94-1; 2-octanone, 111-13-7; acetophenone, 98-86-2; benzaldehyde, 100-52-7; benzoic acid, 65-85-0; *p*-methylbenzaldehyde, 104-87-0; *p*-nitrobenzaldehyde, 555-16-8; *p*-bromobenzaldehyde, 1122-91-4; 1-decanoic acid, 334-48-5; 1-octanoic acid, 124-07-2; 1-heptanoic acid, 111-14-8; 1-butanoic acid, 107-92-6; benzyl benzoate, 120-51-4; 1-octen-3-ol, 3391-86-4; 1-octen-3-one, 4312-99-6.

Synthesis of Triarylbenzenes via Tandem Aryne Reactions of Aryl Grignards with Polyhalobenzenes

Tirthankar Ghosh and Harold Hart*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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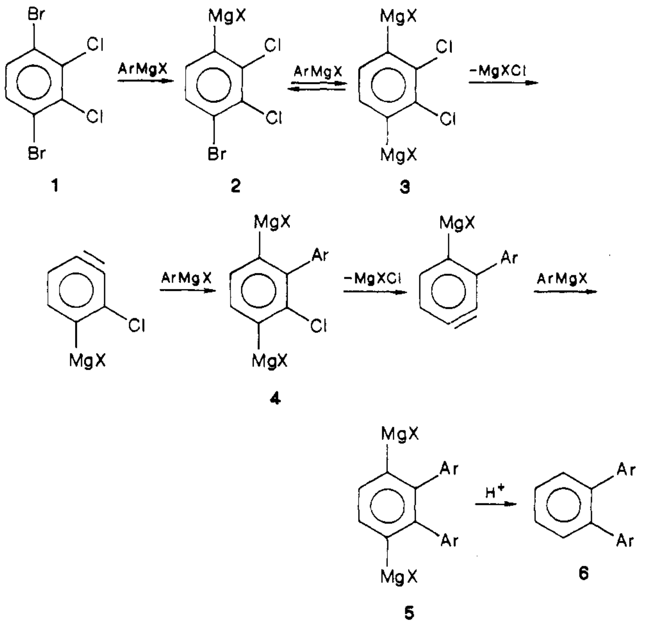
Aryl Grignards react with 1,2,3,4-tetrahalobenzenes to give primarily (2,3,4-triarylphenyl)magnesium halides. The mechanism involves Grignard exchange at one of the "outer" halogens followed by three cycles of magnesium halide loss and regioselective capture of the resulting aryne by the aryl Grignard agent (Scheme II).

Introduction

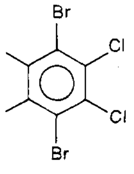
The use of multi-aryne reactions as a synthetic tool for multiple carbon–carbon bond constructions to an arene ring has now been well established. Recently we described general syntheses of biaryls[1] (from 1,2-dihalobenzenes), *p*-terphenyls[1] (from 1,2,4,5-tetrahalobenzenes), *m*-terphenyls[2] (from 1,2,3-trihalobenzenes), and 1,2,4,5-tetraarylbenzenes[3] (from hexahalobenzenes). A similar one-pot synthesis of *o*-terphenyls is lacking. We imagined that such a synthesis might be possible from an appropriate 1,2,3,4-tetrahalobenzene if the reaction were to proceed via a 1,4-diGrignard intermediate (Scheme I).

According to our earlier work, exchange should occur predominantly at Br instead of Cl to give first **2** and then **3**. Assuming that 1,4-diGrignards will be preferred over 1,3-diGrignards, the regiochemistry should be as shown, giving **6**.

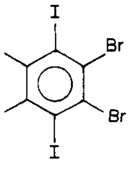
Scheme I



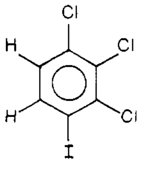
Here we report on our first efforts in this area. Instead of **1**, we used the more easily synthesized dimethyl analogues **7**[4] and **8**,[5] together with the trichloroiodobenzene **9**. Although the desired *o*-terphenyl synthesis was not achieved as anticipated by Scheme I, the results are novel and useful.



7



8



9

Results

Heating **7** at reflux with 5–8 equiv of phenylmagnesium bromide followed by aqueous quench gave 1,2-dimethyl-3,4,5-triphenylbenzene (**10**) in 40% yield, together with 5% of the 1,3-diaryl derivative **11**.[6] Although ^1H NMR

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[1] Hart, H.; Harada, K.; Du, C-J. F. *J. Org. Chem.* **1985**, *50*, 3104.

[2] Du, C-J. F.; Hart, H.; Ng, D.K.-K. *J. Org. Chem.* **1986**, *51*, 3162.

[3] Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524.

[4] Hinkel, L. E.; Ayling, E. E.; Walters, T. M. *J. Chem. Soc.* **1934**, 283.

[5] Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427.

[6] Although we were not able to obtain a pure sample of **11** from this reaction, its ^1H NMR spectrum was identical with that of the sample isolated in the reaction of **8** with phenylmagnesium bromide at 25 °C.