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Studies on Transition-Metal Oxo and Nitrido Complexes. 13.[1] Perruthenate and Ruthenate Anions as Catalytic Organic Oxidants

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The $[RuO_4]^-$ ion can be generated in aqueous base at pH 11 from aquated ruthenium trichloride with excess bromate, and this reagent will catalytically oxidize primary alcohols, activated alkyl halides, aldehydes, 1,2-diols, and nitroalkanes to carboxylic acids, while secondary alcohols and secondary halides are oxidized to ketones, bromate being the cooxidant. These oxidations are compared with those effected catalytically by *trans*-$[Ru(OH)_2O_3]^{2-}$ in aqueous base at pH 14 with persulfate as cooxidant. A new preparation for organic-soluble salts of $[RuO_4]^-$ avoiding the use of RuO_4 is described.

Oxo complexes of ruthenium are effective catalysts for the selective oxidation of various organic substrates.[2] Thus the ruthenate ion *trans*-$[Ru(OH)_2O_3]^{2-}$, which is stable above pH 12 in aqueous base,[3-5] with persulfate as cooxidant will oxidize primary alcohols to carboxylic acids and secondary alcohols to ketones;[6,7] the perruthenate ion $[RuO_4]^-$, which is stable from pH 8 to 12 in aqueous base,[3-5] will also effect such oxidations stoichiometrically in solution.[6] The organic-soluble "TPAP" ((n-Pr_4N)$[RuO_4]$) with N-methylmorpholine N-oxide is an efficient selective catalyst for converting primary alcohols to aldehydes and secondary alcohols to ketones.[8]

Here we report a simple means of generating $[RuO_4]^-$ in aqueous base and using this catalytically with BrO_3^- as cooxidant. Comparative studies on *trans*-$[Ru^{VI}(OH)_2O_3]^{2-}$ with persulfate as cooxidant are also reported, notwithstanding the necessary pH differences of the solutions used, since differences in reactivity and oxidative selectivity might be expected between ruthenium(VII) and ruthenium(VI). The oxidation of activated alkyl halides and of nitro compounds by $[RuO_4]^-/BrO_3^-$ and by *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ in aqueous base is reported for the first time, and the results compared for the two reagents.

Results

(a) The Perruthenate Anion $[RuO_4]^-$. The tetrahedral[9] $K[RuO_4]$ is normally prepared from *trans*-$[Ru(OH)_2O_3]^{2-}$ and chlorine in base.[6] In aqueous base it stoichiometrically oxidizes primary alcohols to carboxylic acids and secondary alcohols to ketones but can cause double bond cleavage.[5,6,10]

We find that $[RuO_4]^-$ can be conveniently generated by reaction of $RuCl_3{\cdot}nH_2O$ or $RuO_2{\cdot}nH_2O$ with excess $NaBrO_3$ in 1 M Na_2CO_3 solution. From this both (n-Pr_4N)$[RuO_4]$ and $(PPh_4)[RuO_4]$ can be isolated in high yields, better preparations than previously reported[1,11] in that the use of RuO_4 is avoided. By using a low concentration of ruthenium (1.5×10^{-3} M $RuCl_3{\cdot}nH_2O$) and 1 M $NaBrO_3$ in 1 M Na_2CO_3 solution at pH 11, $[RuO_4]^-$ is rapidly generated and the solution is a catalytic oxidant, bromate functioning as cooxidant. The presence of $[RuO_4]^-$ is shown by the electronic spectrum of the yellow-green solution, and the absorption maxima and molar extinction coefficients of the $[RuO_4]^-$ thus generated are in reasonable agreement with those given for the ion by Connick and Hurley;[3] no bands due to $[RuO_4]$ or *trans*-$[Ru(OH)_2O_3]^{2-}$ were observed. Such solutions are stable for over 1 year. All the oxidations reported in Table I were also carried out in the absence of ruthenium (i.e. in basic bromate only), and in all cases the degree of oxidation was zero or small over the quoted times. The $[RuO_4]^-$ anion can also be generated if 0.7 M persulfate replaces bromate but is not then a catalytic oxidant; furthermore although the absorption maxima are in the correct positions for $[RuO_4]^-$, the molar extinction coefficients are low. Sodium bismuthate can be used as a cooxidant in 1 M aqueous hydroxide with $RuCl_3{\cdot}nH_2O$ to produce $[RuO_4]^-$, but its efficacy is limited by the low solubility of $NaBiO_3$ and the catalytic turnovers are low. The use of bromate to oxidize hydrated ruthenium trichloride or ruthenium dioxide has been reported,[12,13] in some cases[13] in basic media; $[RuO_4]^-$ was not identified as the oxidizing species though it may indeed have been involved. Although it has been suggested[14] that $[RuO_4]^-$ can be generated from a biphasic KIO_4–RuO_2–Na_2CO_3–benzyltriethylammonium

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Table I. Catalytic Oxidations Using Perruthenate $[RuO_4]^-/BrO_3^-$ and Ruthenate *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$

	aqueous					phase transfer				
		perruthenate^a		ruthenate^b			perruthenate^a		ruthenate^b	
substrate	products	yield (%) (TO)^c	time (h)	yield (%) (TO)^c	time (h)	products	yield (%) (TO)^c	time (h)	yield (%) (TO)^c	time (h)
Alcohols										
benzyl	benzoic acid	99 (75)	1.5	97 (40)	1.5	benzaldehyde	60 (48)	1.3	50 (16)	1.3
p-methoxybenzyl	*p*-anisic acid	97 (68)	4	99 (37)	4	*p*-anisaldehyde	93 (68)	4	77 (25)	4
o-methylbenzyl	*o*-toluic acid	73 (55)	4	70 (23)	4	*o*-tolualdehyde	53 (41)	3.5	38 (12)	3.5
3,4-dimethoxybenzyl	3,4-dimethoxybenzoic acid	87 (66)	4	90 (31)	4	3,4-dimethoxybenzaldehyde	88 (66)	4	93 (30)	4
p-nitrobenzyl	*p*-nitrobenzoic acid	85 (62)	4	81 (27)	4	*p*-nitrobenzaldehyde	23 (16)	4		
piperonyl	piperonylic acid	85 (62)	4	63 (29)	4	piperonal	88 (63)	4	96 (32)	4
cinnamyl	cinnamic acid^d	63 (47)	6	90 (34)	6	cinnamaldehyde	50 (37)	5	72 (23)	6
α-tetralol	α-tetralone	84 (115)	2	73 (25)	3	α-tetralone	88 (64)	2	33 (11)	3
benzhydrol	benzophenone	70 (50)	3	40 (14)	4	benzophenone	35 (26)	3	15 (6)	4
cycloheptanol	cycloheptanone	45 (33)	4	71 (24)	4	cycloheptanone	53 (42)	3	8 (3)	3
Aldehydes										
benzaldehyde	benzoic acid	96 (143)	1	95 (43)	1					
4-methoxybenzaldehyde	*p*-anisic acid	67 (96)	5	92 (36)	5					
cinnamaldehyde	cinnamic acid^d	38 (54)	5	99 (34)	5					
Halides										
benzyl chloride	benzoic acid	18 (13)	6	43 (17)	6					
benzyl bromide	benzoic acid	77 (56)	6	96 (39)	4					
p-methoxybenzyl chloride	*p*-anisic acid	92 (74)	5	89 (31)	6	*p*-anisaldehyde	80 (62)	4.5	65 (21)	4.5
α-bromo-*p*-xylene	*p*-toluic acid	50 (36)	6	86 (35)	6					
cinnamyl chloride	cinnamic acid^d	40 (29)	6	88 (26)	7	cinnamaldehyde	18 (13)	5.5		
cinnamyl bromide	cinnamic acid^d	62 (45)	6	52 (20)	7	cinnamaldehyde	6 (4)	5.5		
2,6-dichlorobenzyl bromide	2,6-dichlorobenzoic acid	11 (7)	6	11 (4)	7					
1-iodobutane	butyric acid	7 (5)	6	18 (6)	6.5					
1-bromoethyl benzene	acetophenone	52 (46)	6	62 (28)	6	acetophenone	19 (14)	5		
diphenyl bromomethane	benzophenone	22 (16)	6	11 (2)	6					
Diols										
hydrobenzoin	benzoic acid	75 (124)	3	83 (58)	3	benzil	65 (93)	3		
1,2-cyclooctanediol	suberic acid	40 (28)	4	50 (22)	4	1,2-cyclooctanone	6 (4)	3		
trans-cyclohexanediol	adipic acid	89 (64)	4	18 (6)	4	adipic acid	37 (27)	4		
cis-cyclohexanediol	adipic acid	72 (52)	5	14 (5)	4	adipic acid	25 (18)	4		
Nitroalkanes										
nitroethane	acetic acid	90 (69)	5	20 (8)	5					
nitropropane	propionic acid	95 (27)	5	26 (11)	5					
nitrobutane	butyric acid	90 (68)	5	71 (27)	5					
nitropentane	pentanoic acid	33 (25)	5	96 (36)	5					
nitrohexane	hexanoic acid	31 (23)	5	98 (33)	5					

^{a} 1.35×10^{-3} M $RuCl_3{\cdot}3H_2O$; 1 M aqueous $NaBrO_3$; 1 M Na_2CO_3. ^{b} 6×10^{-4} M $RuCl_3{\cdot}3H_2O$; 0.05 M aqueous $K_2S_2O_8$; 1 M KOH. ^{c} Catalytic turnover. ^{d} Benzoic acid formed by $[RuO_4]^-/BrO_3^-$; cinnamic formed by *trans*-$[Ru(OH)_2O_3]^{2-}$.

chloride mixture in 1:1 chloroform–water, our electronic spectral measurements on such solutions suggest that RuO_4 rather than $[RuO_4]^-$ is present.

(b) The Ruthenate Anion *trans*-$[Ru(OH)_2O_3]^{2-}$. We have earlier shown[6,7] that *trans*-$[Ru(OH)_2O_3]^{2-}$ in aqueous solution can be made from 6.0×10^{-4} M $RuCl_3{\cdot}nH_2O$ in 5.2×10^{-2} M $K_2S_2O_8$ and 1 M KOH (pH = 14). At this pH ruthenate is relatively stable[5] and such solutions will stoichiometrically[15] or catalytically[6,7] oxidize primary alcohols to carboxylic acids and secondary alcohols to ketones. The X-ray crystal structures of *trans*-$K_2[Ru(OH)_2O_3]$[16] and *trans*-$Ba[Ru(OH)_2O_3]$[17] show that these complexes contain the trigonal bipyramidal *trans*-$[Ru(OH)_2O_3]^{2-}$ anion, while the anion in $Cs_2[RuO_4]$ is tetrahedral.[18] We find that the *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent will oxidize primary activated alkyl halides to carboxylic acids and secondary alkyl halides to ketones. *trans*-$[Ru(OH)_2O_3]^{2-}$ can also be generated from $RuCl_3{\cdot}nH_2O$ (2.3×10^{-4} M) with $NaBrO_3$ (0.16 M) in 1.6 M KOH solution or from $RuCl_3{\cdot}nH_2O$ (2.3×10^{-4} M) in 1 M KOH with 0.2 M sodium peroxoborate ($Na_2[B_2(O_2)_2(OH)_4]{\cdot}6H_2O$). However, the former solution shows no advantages over *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$, while the peroxoborate reagent is unstable and a poor catalytic oxidant.

(c) Catalytic Oxidation by $[RuO_4]^-/BrO_3^-$ and by *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$. Both $[RuO_4]^-/BrO_3^-$ and *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ function as catalysts for the substrates below (see Table I), bromate and persulfate respectively functioning as cooxidants. Both reagents are aesthetically and practically attractive in that they are self-indicating, the yellow-green color of $[RuO_4]^-$ and the orange of *trans*-$[Ru(OH)_2O_3]^{2-}$ becoming black (probably due to the presence of colloidal RuO_2) on addition of substrate and returning to their original colors when the oxidation reaction is complete.

(i) Alcohols. Primary alcohols are oxidized to carboxylic acids

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by $[RuO_4]^-/BrO_3^-$ or *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ (Table I). With cinnamyl alcohol, the latter reagent gives cinnamic acid only, while $[RuO_4]^-/BrO_3^-$ cleaves the double bond and the major product is benzoic acid, though some cinnamaldehyde was also detected. For secondary alcohols aqueous $[RuO_4]^-$ seems to be a more effective oxidant than *trans*-$[Ru(OH)_2O_3]^{2-}$. Larger scale oxidations can be effected; thus with $[RuO_4]^-/BrO_3^-$, 5.4 g of benzyl alcohol gives 5.49 g (90%) of benzoic acid using 0.09 g of $RuCl_3{\cdot}nH_2O$ over a 24-h period. *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ oxidizes 4-nitrobenzaldehyde and benzyl alcohol to the corresponding acids under relatively large-scale conditions;[7] it also oxidizes cinnamaldehyde (6.6 g) in 20 h to cinnamic acid (7.12 g, 97%). Under phase-transfer conditions (1:1 water–dichloroethane) using Aliquat 336 (tricaprylmethylammonium chloride), extraction of the nonaqueous layer after oxidation with either of the reagents gives the aldehyde in high yield; in the case of cinnamyl alcohol, cinnamaldehyde is produced by both.

(ii) Aldehydes and Diols. Aldehydes, as expected, are oxidized to carboxylic acids by both reagents, while cinnamaldehyde is cleaved to benzoic acid by $[RuO_4]^-/BrO_3^-$. In aqueous solution $[RuO_4]^-/BrO_3^-$ oxidizes diols to dicarboxylic acids; under phase-transfer conditions we could not isolate the diketo compounds but did obtain dicarboxylic acids. The *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent is less effective for these reactions than is $[RuO_4]^-/BrO_3^-$.

(iii) Alkyl Halides. The best known procedures for oxidation of halides to aldehydes, acids, or ketones are the noncatalytic Sommelet or Kornblum reactions,[19] and *N*-methylmorpholine *N*-oxide will also effect such oxidations.[20] Both aqueous $[RuO_4]^-/BrO_3^-$ and *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ will convert activated primary alkyl halides to carboxylic acids and activated secondary halides to ketones. Under large-scale conditions *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ oxidizes benzyl bromide (7.6 g) in 40 h to benzoic acid (4.07 g, 75%) with 0.19 g of $RuCl_3{\cdot}nH_2O$; in the case of $[RuO_4]^-/BrO_3^-$ benzyl bromide (5.0 g) is oxidized to 2.43 g (68%) of benzoic acid with 0.08 g of $RuCl_3{\cdot}nH_2O$ in 40 h.

(iv) Nitro Compounds. The oxidation of primary nitroalkanes to aldehydes and secondary nitroalkanes to ketones is normally effected by the Nef reaction;[21] ozonolysis may also be used,[22] but *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ has been used on one occasion for the production of a ketone.[23] We find that both the perruthenate and ruthenate reagents oxidize primary nitro compounds to carboxylic acids; under phase-transfer conditions no aldehydes could be detected in the organic phase.

Discussion

The formation of $[RuO_4]^-$ and of *trans*-$[Ru(OH)_2O_3]^{2-}$ by oxidation of $RuO_2{\cdot}nH_2O$ or $RuCl_3{\cdot}nH_2O$ by strong oxidants in base is not surprising, since the stabilities of these oxo complexes in base has been well established,[3–5] and it has been shown that bromate[12,13] and persulfate[6,7,24] will oxidize lower oxidation state ruthenium compounds. From our earlier work on the aqueous ruthenate reagent[6,7] and on the $[RuO_4]^-$/NMO system[8] it seems likely that initial reduction to ruthenium(IV), probably as RuO_2, occurs when the substrate is added to the reagents, and this is reoxidized by the cooxidant. In agreement with this we find that hydrated RuO_2 can be used in place of $RuCl_3{\cdot}nH_2O$ to produce these reagents with bromate at pH 11 or persulfate at pH 14, respectively.

The range of relatively efficient catalytic oxidations effected by $[RuO_4]^-/BrO_3^-$ and by *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ is unexpected and shows some interesting features. It has been established that $(n\text{-}Pr_4N)[RuO_4]$ and $(n\text{-}Bu_4N)[RuO_4]$ will oxidize primary alcohols to aldehydes but not to carboxylic acids in nonaqueous solutions either catalytically[8a–c] or stoichiometrically.[8d,e] Oxidations of primary alcohols by $[RuO_4]^-/BrO_3^-$ to carboxylic acids in aqueous base probably proceed via an aldehyde intermediate (indeed, by using two-phase systems we were able to isolate some of the aldehydes). The water present would produce the aldehyde hydrate: formation of the latter is known to be a prerequisite for aldehyde oxidation to carboxylic acids.[25] The slightly greater effectiveness of both reagents at oxidizing primary as against secondary alcohols has been observed for other ruthenium-based oxidants.[26] Cleavage of the olefinic double bond in cinnamyl alcohol by the $[RuO_4]^-/BrO_3^-$ reagent and the lack of such cleavage when *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ is used accords with the observation[5] that, under stoichiometric conditions, perruthenate in aqueous base cleaves oleic acid while ruthenate does not, consistent perhaps with the higher oxidation state of ruthenium in the former. The mechanism of the reaction between $[RuO_4]^-$ and alkenes has been studied,[27] as has the stoichiometric reaction of $(n\text{-}Pr_4N)[RuO_4]$ with propan-2-ol.[8d] Cleavage of diols such as *erythro*-9,10-dihydroxystearic acid by perruthenate (and, less effectively, by ruthenate) has also been noted,[5] both under stoichiometric but not catalytic conditions; both our reagents cleave diols, again with perruthenate being more effective than ruthenate.

The catalytic oxidation of activated (benzylic) alkyl halides to carboxylic acids or ketones and of primary nitro compounds to carboxylic acids is an unusual feature of these systems. We have shown that the oxidation of alkyl halides to carboxylic acids is catalyzed by some high oxidation state periodato complexes;[28] oxidation of a nitrolactone to a carbonyl compound by *trans*-$[Ru(OH)_2O_3]^{2}/S_2O_8^{2-}$ has been noted by Corey et al.,[23] and cerium(IV) will also accomplish the Nef reaction, albeit stoichiometrically in the latter case,[29] but for both types of oxidation such metal-catalyzed reactions are still rare. For reactions of alkyl halides and nitro compounds the ruthenate reagent is more effective than perruthenate, and it seems likely that this arises from the higher pH (i.e. 14) of the former reagent, which assists more effectively the removal of hydrohalic acid formed in the reaction. As with the alcohol oxidations, cinnamyl chloride and bromide are cleaved at the olefinic double bond to give benzoic acid by $[RuO_4]^-/BrO_3^-$ whereas there is no such cleavage by the milder *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent, cinnamic acid being the product.

Experimental Section

Materials. $RuCl_3{\cdot}nH_2O$ ($n \sim 3$) was loaned by Johnson Matthey Ltd. Other reagents were obtained from Aldrich or BDH.

Perruthenate–Bromate Reagent $[RuO_4]^-/BrO_3^-$. Anhydrous Na_2CO_3 (0.8 g, 7.5 mmol) was dissolved in water (7.5 cm^3) and $NaBrO_3$ (1.2 g, 8 mmol) added to produce a 1 M carbonate buffer solution; $RuCl_3{\cdot}nH_2O$ (0.003 g, 0.011 mmol) in water (1 cm^3) was then introduced with stirring. The color changed to yellow green; the pH was 11.3. Electronic spectrum [nm (ϵ/dm^3 mol^{-1} cm^{-1})]: 378 (2527) and 310 (2608).

$(n\text{-}Pr_4N)[RuO_4]$ (1; TPAP) and $(PPh_4)[RuO_4]$ (2). Anhydrous Na_2CO_3 (1.58 g, 15 mmol) and $NaBrO_3$ (6.0 g, 50 mmol) in water (20 cm^3) and $RuCl_3{\cdot}nH_2O$ (0.13 g, 0.5 mmol) in water (5 cm^3) were stirred together until the color became yellow-green. $n\text{-}Pr_4N(OH)$ (0.102 g, 0.5 mmol) or PPh_4Cl (0.18 g, 0.5 mmol) was added with stirring, the deep green

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precipitate was extracted into alcohol-free dichloromethane (50 cm^3), and the solution was dried over anhydrous Na_2CO_3, concentrated in vacuo, and recrystallized by adding CCl_4.

Data for **1** are as follows. Yield: 0.17 g, 0.49 mmol (99%). Anal. Found: C, 40.5; H, 8.2; N, 3.7. Calcd for $C_{12}H_{28}NO_4Ru$: C, 41.0; H, 8.0; N, 4.0. IR (ν_{max}/cm^{-1}): 836 (strong) ($\nu^{as}(RuO_4)$). Electronic spectrum in CH_2Cl_2 [nm (ϵ/dm^3 mol^{-1} cm^{-1})]: 378 (2174) and 310 (2454).

Data for **2** are as follows. Yield: 0.24 g, 0.47 mmol (95%). Anal. Found: C, 56.9; H, 4.0. Calcd for $C_{24}H_{20}O_4PRu$: C, 57.1; H, 4.0. IR (ν_{max}/cm^{-1}): 832 (strong) ($\nu^{as}(RuO_4)$). Electronic spectrum in CH_2Cl_2 [nm (ϵ/dm^3 mol^{-1} cm^{-1})]: 379 (2260) and 318 (2480).

Ruthenate–Persulfate Reagent *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$. To 1 M KOH (50 cm^3) containing $K_2S_2O_8$ (0.7 g, 2.6 mmol) was added $RuCl_3 \cdot nH_2O$ (0.008 g, 0.03 mmol) in water (3 cm^3), and the mixture was stirred until the orange ruthenate color appeared; the pH was 13.9. Electronic spectrum [nm (ϵ/dm^3 mol^{-1} cm^{-1})]: 466 (1420) and 386 (989).

Catalytic Oxidations. (i) Aqueous Conditions. The substrate (1 mmol) was added with stirring to the $[RuO_4]^-/BrO_3^-$ solution (10 cm^3) or *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ (50 cm^3) solution at room temperature for the times listed in Table I. In most cases the oxidations are self-indicating; i.e. the yellow-green color of $[RuO_4]^-$ or the orange of *trans*-$[Ru(OH)_2O_3]^{2-}$ reappears when oxidation is complete. The reaction mixture was extracted with diethyl ether (3 × 25 cm^3), the ethereal layer dried over anhydrous Na_2SO_4, and the aldehyde or ketone content quantified with 2,4-dinitrophenylhydrazine. The alkaline aqueous layer was acidified with H_2SO_4 to pH 2, extracted with ether (3 × 25 cm^3), and dried to give the acid. In the case of the $[RuO_4]^-/BrO_3^-$ system solid anhydrous Na_2SO_3 was added to the aqueous acidic solution to prevent interference by bromine with the products.

(ii) Phase-Transfer Conditions. Solutions of the $[RuO_4]^-/BrO_3^-$ or *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagents were added to the substrate (1 mmol) in 1,2-dichloroethane (1:1 by volume), and Aliquat 336 (0.2 g) was added. The reaction mixture was stirred at room temperature for the times listed in Table I, extracted with ether (3 × 25 cm^3), and treated as above.

Instrumentation. IR spectra were measured on a Perkin-Elmer 1720 FTIR, NMR spectra on a Bruker WM-250, and electronic spectra on a Perkin-Elmer Lambda 2 UV/vis spectrophotometer.

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