After the mixture was stirred at room temperature for 1–4 h (monitor via TLC), saturated aqueous ammonium chloride was added. The resulting solution was extracted twice with ether and once with pentane. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo.

For LiS-*t*-Bu. Purification via preparative TLC (same plates as described above) using 1/3 ether–pentane (three developments) was carried out. The spectral data were as follows: IR (neat) 2955, 2860, 1735, 1458, 1432, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3 H, CO_2CH_3), 3.72 (s, 3 H, CO_2CH_3), 1.7–2.6 (m, 7 H, ring), 1.3 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 170.1, 168.9, 63.6, 53.9, 53.0, 35.8, 33.3, 30.7, 23.4; low-resolution mass spectrum, *m/e* 274, 217, 187, 158, 145, 126, 113, 95, 57; exact mass calcd for $C_{13}H_{22}SO_4$ 274.1239, found 274.1238.

For NaCH(CO_2CH_3)$_2$[10] the spectral data were as follows: IR (neat) 2955, 2850, 1735, 1438 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3 H, CO_2CH_3), 3.72 (s, 3 H, CO_2CH_3), 3.38 (t, 1 H, $J = 8$ Hz, C**H**(CO_2CH_3)$_2$), 1.6–2.6 (m, 7 H, ring); ^{13}C NMR ($CDCl_3$) δ 168.9, 62.1, 54.1, 52.5, 52.2, 35.6, 22.2.

For KCN the spectral data were as follows: IR (neat) 2955, 2870, 2280, 1735, 1450, 1432 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3 H, CO_2CH_3), 3.78 (s, 3 H, CO_2CH_3), 1.7–2.8 (m, 7 H, ring); ^{13}C NMR ($CDCl_3$) δ 169.9 (CN), 53.2, 53.1, 35.8, 33.4, 30.8, 23.5; exact mass calcd for $C_{10}H_{14}NO_4$ [$(M + 1)^{+\cdot}$; as is sometimes the case for nitriles, the $M^{+\cdot}$ peak was not observed while the $(M + 1)^{+\cdot}$ was observed[11]) 212.0877, found 212.0914. High-resolution mass spectra on several key fragments include the following [*m/e* (relative intensity)]: calcd for $C_7H_8NO_4$ 170.0453 (100), found 170.0475; calcd for $C_2H_3O_2$ 59.0132 (95), found 59.0157; calcd for C_5H_7 67.0547 (79), found 67.0588; calcd for $C_9H_{10}NO_3$ 180.0661 (48), found 180.0695.

L-Selectride Reactions with 1b and 2.[14] To a two-necked round bottomed flask equipped with a nitrogen inlet and a magnetic stirring bar was added 1.1 equiv of L-Selectride (1 M solution in THF); the flask was then cooled to −78 °C. After 15 min, a 1 M solution of the substrate dissolved in THF was added by using a syringe pump over 30–45 min. The cooling bath was then removed and the solution was then raised to either 0 °C (for **1b**) or reflux (for **2**) for 1 h after which time the reaction was quenched by the addition of saturated aqueous ammonium chloride. After extraction of the aqueous layer with ether, the combined organic material was washed two times with brine, dried ($MgSO_4$), and concentrated in vacuo. The products were purified by using gravity-flow chromatography on silica gel (E. Merck, 70–230 mesh; 20% ether–pentane). For **2**:[12] IR (neat) 2955, 1720, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 6 H, CO_2CH_3), 1.8–2.2 (m, 4 H, C**H**$_2$C(CO_2CH_3)$_2$C**H**$_2$), 1.26–1.73 (m, 6 H, remaining ring H's); GC/MS *m/e* (relative intensity) 200, 169, 145, 132, 113, 108, 80 (100), 59. For **1b**:[13] IR (neat) 2955, 1730, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H, CO_2CH_3), 1.95–2.42 (m, 4 H, C**H**$_2$C(CO_2CH_3)$_2$C**H**$_2$), 1.46–1.93 (m, 4 H, remaining ring H's); ^{13}C NMR ($CDCl_3$) δ 172.3, 59.8, 51.7, 34.0, 24.8; GC/MS (parent not observed) *m/e* (relative intensity) 155, 145 (100), 126, 113, 95, 67, 59.

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Registry No. 1b, 79917-27-4; **2**, 79917-28-5; 4-bromobutanal, 38694-47-2; 5-bromopentanal, 1191-30-6; 4-bromobutyronitrile, 5332-06-9; 5-bromovaleronitrile, 5414-21-1; dimethyl malonate, 108-59-8; 1,1-cyclohexane dicarboxylic acid dimethyl ester, 72963-31-6; 2-cyano-1,1-cyclohexane dicarboxylic acid dimethyl ester, 79917-29-6; 2-[[bis(methoxycarbonyl)]methyl]-1,1-cyclohexane dicarboxylic acid dimethyl ester, 79917-30-9; 2-(*tert*-butylthio)-1,1-cyclohexane dicarboxylic acid dimethyl ester, 79917-31-0; 1,1-cyclopentane dicarboxylic acid dimethyl ester, 74090-15-6; 2-cyano-1,1-cyclopentane dicarboxylic acid dimethyl ester, 79917-32-1; 2-[[bis(methoxycarbonyl)]methyl]-1,1-cyclopentane dicarboxylic acid dimethyl ester, 79917-33-2; 2-(*tert*-butylthio)-1,1-cyclopentane dicarboxylic acid dimethyl ester, 79917-34-3; L-Selectride, 38721-52-7; KCN, 151-50-8; NaCH(CO_2CH_3)$_2$, 18424-76-5; *t*-BuSNa, 29364-29-2; *t*-BuSLi, 16203-42-2.

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A New Triphasic Solid–Solid–Liquid Catalytic System for the Inexpensive and Selective Oxidation of Secondary Alcohols by Calcium Hypochlorite

Michel Schneider, Jean-Victor Weber, and Pierre Faller*

Laboratoire de Chimie Organique, Université de Metz, Ile du Saulcy, 57000 Metz, France

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In the past decade, biphasic liquid–liquid and solid–liquid reactions have had a remarkable development, leading to the currently classical notion of "phase transfer catalyst" or "ionophore"; comprehensive theoretical interpretation has also been offered.[1] Among the four possible condensed triphasic systems, liquid–liquid–solid and liquid–solid–solid are of more recent and growing interest (see ref 2 and 3 and references mentioned herein), although they are not fully grasped yet. We report here an additional example of such a triphasic solid–solid–liquid catalysis, applied to the oxidation of alcohols by calcium hypochlorite in the presence of a solid polymer in a nonaqueous medium.

Sodium hypochlorite in acetic acid[4] or in a biphasic water–solvent system[5] has proven to be an efficient and economically interesting oxidation agent, although some difficulties may occur for the extraction of water-soluble ketones. The alternative proposed here, like previous research on the $KMnO_4$–$CuSO_4$ $(H_2O)_5$ pair,[3] makes it possible to work in an organic medium and to isolate the oxydation products through easy filtration and evaporation of the solvent. We used commercial calcium hypochlorite[6] in various solvents (CH_2Cl_2, CCl_4, Et_2O, CH_3CO_2Et) and catalytic amounts of a "hypochlorite" resin obtained from commercial IRA 900 (technical details are given in the Experimental Section).

Results are summarized in Table I. A separate run without a catalyst (entry 1) demonstrates a low activity of calcium hypochlorite alone, owing probably to the presence of traces of water.[3] Yields are not improved when working in the presence of the initial ammonium chloride

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Table I. Oxidation of Alcohols with Calcium Hypochlorite

entry	starting alcohol	catalyst/solvent/time (h)	ketone formed	% yield
1	cycloheptanol	none/CH_2Cl_2/12	cycloheptanone	24
		IRA 900, Cl^-/CCl_4/3		
		IRA 900, OH^-/CCl_4/3	cycloheptanone	trace
		IRA 900, AcO^-/CCl_4/3		
		IRA 900, OCl^-/CCl_4/3	cycloheptanone	85
		IRA 900, OCl^-/CH_2Cl_2/3	cycloheptanone	92
		IRA 900, OCl^-/ethyl acetate/3	cycloheptanone	85
		IRA 900, OCl^-/ethyl ether/3	cycloheptanone	85
2	cycloheptanol + *n*-heptanol	IRA 900, OCl^-/CCl_4/3	cycloheptanone	85
			n-heptanol	98
3	cycloheptanol	recovered IRA 900, OCl^-		
		2nd run/CCl_4/3	cycloheptanone	85
		3rd run/CCl_4/3		85
4	cyclohexanol	IRA 900, OCl^-/CCl_4/3	cyclohexanone	80
	cyclopentanol	IRA 900, OCl^-/CCl_4/3	cyclopentanone	90
	2-propanol	IRA 900, OCl^-/ethyl ether/3	acetone	95
5	2,6-dimethylcyclohexanol	IRA 900, OCl^-/CCl_4/3	2,6-dimethylcyclohexanone	60[a]
	menthol	IRA 900, OCl^-/CCl_4/3	menthone	28[a]
		IRA 900, OCl^-/CCl_4/12		92[a]

[a] Plus nonreacted alcohol.

polymer or with its hydroxy or acetate forms obtained by anion exchange. Competitive reaction between cycloheptanol and *n*-heptanol (entry 2) results in the oxidation of the secondary alcohol, demonstrating the good selectivity of the method and excluding the inhibition effect reported elsewhere.[3] In contrast with the results under homogeneous phase oxidation by sodium hypochlorite,[4] steric and geometric factors may affect rate constants (entry 5). It must be emphasized finally that the catalyst recovered, without any regeneration process, could be used again several times with no loss of activity (entry 3).

The theoretical aspect of this triphasic catalysis and the possibility of it being extended to other transformations is currently being investigated.

Experimental Section

Reaction mixtures were analyzed by VPC on a Perkin-Elmer Model Sigma 3B flame-ionization instrument, using a 3% Carbowax on a Chromosorb Q column ($^1/_8$ in. × 2 m). Appropriate response factors relative to the chlorobenzene as internal standard were determined for each constituent of the samples injected.

For spectroscopic determination we used a Perkin-Elmer R 12 A (NMR) and a Beckman Acculab (IR).

Starting alcohols were purified by distillation or recrystallization and purity was controlled by VPC. Pure grade solvents, commercial sodium hypochlorite solution[7] and calcium hypochlorite[6] were used without further purification.

Preparation of the Resin Catalysts. Thirty milliliters of commercial IRA 900 (Cl^- form)[8] was successively washed with deionized water (200 mL), 2 M aqueous sodium hydroxide (300 mL), deionized water until neutrality, sodium hypochlorite solution (300 mL), deionized water until neutrality, and anhydrous acetone (300 mL) and finally dried in vacuo at room temperature for several hours. The hypochlorite form thus obtained is noted IRA 900, OCl^- in Table I.

Oxidation of the Alcohols. General Procedure. The alcohol (0.01 mol) was slowly added to a well-stirred suspension of 4 g of calcium hypochlorite and 1 g of IRA 900, OCl^- in 25 mL of a suitable solvent, care being taken to keep the temperature below 40 °C. Stirring at room temperature was continued for 3 h. The solution was filtered (when conducted in CCl_4 the supernatent catalyst may be skimmed for further use) and subjected to VPC analysis and solvent distillation. Given yields, for a 3-h reaction time, have not been optimized.

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Registry No. Cycloheptanol, 502-41-0; *n*-heptanol, 111-70-6; cyclohexanol, 108-93-0; cyclopentanol, 96-41-3; 2-propanol, 67-63-0; 2,6-dimethylcyclohexanol, 5337-72-4; menthol, 1490-04-6; cycloheptanone, 502-42-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; acetone, 67-64-1; 2,6-dimethylcyclohexanone, 2816-57-1; menthone, 89-80-5; calcium hypochlorite, 7778-54-3.

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(7) From PROLABO (density 1.22; 3.5–4.4 M).

(8) From Rohm & Haas Co.

Palladium Catalysis as a Means for Promoting the Allylic C-Alkylation of Nitro Compounds

Peter A. Wade,* Scott D. Morrow, and Steven A. Hardinger

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

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Primary and secondary nitro compounds are valuable synthetic intermediates with one widely recognized limitation. The monoanions derived from them are more prone to alkylate on oxygen rather than on carbon in reactions with most alkyl halides.[1] It seems that virtually all nitro compounds suffer from this liability and that it is particularly pronounced for nitroalkanes. Ethyl α-nitroacetate does undergo some C-alkylation, but even here yields are rarely over 60%.[1,2] We have recently shown that (phenylsulfonyl)nitromethane undergoes C-alkylation, again in somewhat limited yield for simple primary alkyl iodides and benzylic bromides.[3]

Perhaps the most general way to circumvent O-alkylation of a primary nitro compound is to alkylate its α,α-dianion.[4] It is also possible to carry out $S_{RN}1$ reactions

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