nol–water (1:1) containing 3 g of NaOH. Sodium borohydride (2.5 g, 65.1 mmol) was added to the solution with stirring at room temperature. After 2 h, the reaction was worked up by acidifying with concentrated HCl to pH 1 and extracting with 2 × 200 mL of ether. The combined extracts were washed with 100 mL each of 10% $NaHCO_3$ and saturated brine and then dried over anhydrous $MgSO_4$ to yield 3.20 g of liquid residue after removal of solvents. Distillation (Kugelrohr) of the crude product gave 3.01 g (91% yield) of **4**: bp 108–110 °C/0.8 mm; IR ($CHCl_3$) 1785, 1745, 1640, 1040, 1030, 895, and 860 cm^{-1}; NMR ($CDCl_3$) δ 5.82 (q, J = 2 Hz, 1 H), 4.78 (d, J = 2 Hz, 2 H), 3.8 (m, 1 H), 1.2–2.2 (m, 8 H); mass spectrum, *m/e* (relative intensity) 152 (60), 123 (100), 107 (67), 95 (35), 93 (43), 69 (53), 68 (75), 67 (75), 60 (70), 55 (75), 41 (70).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.98; H, 7.95.

Bromination of 4 with *N*-Bromosuccinimide. A 31-mg (0.02-mmol) sample of **4**, 36 mg (0.2 mmol) of NBS (Fisher Chemical Co.), and a small crystal of azobis(isobutyronitrile) were stirred with 2 mL of dry carbon tetrachloride in a 5-mL round-bottom flask fitted with a condenser and a drying tube ($CaSO_4$). The mixture was exposed to a 275-W sun lamp with a filter (Corning no. 7380, $\lambda > 340$ nm) for 45 min. The resulting suspension was filtered and the filtrate evaporated. The solid residue obtained was recrystallized from isopropyl ether–ether to give 34 mg (74% yield) or 3-(1-bromocyclopentyl)-2-butenolide (**5**) as colorless plates: mp 69–70 °C; IR ($CHCl_3$) 1795, 1760, 1635, 1050, 895, and 860 cm^{-1}; NMR ($CDCl_3$) δ 6.00 (t, J = 2 Hz, 1 H), 5.08 (d, J = 2 Hz, 2 H), 1.6–2.5 (m, 8 H); mass spectrum, *m/e* (relative intensity) 231 (0.3), 229 (0.4), 167 (2), 151 (100), 123 (20), 107 (12), 105 (9), 95 (10), 93 (12), 91 (7), 67 (8).

Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.77; H, 4.76; Br, 34.60. Found: C, 46.77; H, 4.86; Br, 34.40.

Bromination of the Anion from 4. To a solution of 0.19 mL (1.1 mmol) of 2,2,6,6-tetramethylpiperidine in 3 mL of dry tetrahydrofuran was added 0.45 mL (1.0 mmol) of *n*-butyllithium solution (2.2 M in hexane).[14] The solution was stirred under N_2 for 1 h at room temperature. A solution of 152 mg (1.0 mmol) of **4** in 0.5 mL of dry tetrahydrofuran was then introduced, and the mixture was stirred for another 1 h. The resulting solution was syringed dropwise into a solution of Br_2 (0.1 mL, 2 mmol) in 1 mL of dry tetrahydrofuran under an N_2 atmosphere. The bromine solution decolorized rapidly with a white precipitate forming. After being stirred for 15 min, the mixture was diluted with 20 mL of ether, washed with 10 mL of 5% HCl, 10 mL of $NaHSO_4$ (10%) solution, and 10 mL of brine, and then dried over anhydrous $MgSO_4$. The crude product obtained after removal of the solvents was chromatographed by TLC ($CHCl_3$–CCl_4, 4:1) to give 155 mg (67% yield) of 4-bromo-3-cyclopentyl-2-butenolide (**6**): bp 85–90 °C/0.6 mm (Kugelrohr); IR ($CHCl_3$)[15] 1795, 1760, 1635, 1020, 875, and 855 cm^{-1}; NMR ($CDCl_3$) δ 6.82 (s, 1 H), 5.95 (d, J = 1 Hz, 1 H), 2.9 (m, 1 H), 1.4–2.3 (m, 8 H); mass spectrum, *m/e* (relative intensity) 231 (3), 229 (3), 151 (100), 137 (9), 135 (9), 133 (8), 123 (8), 95 (6), 67 (80), 55 (39), 41 (75).

Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.77; H, 4.76; Br, 34.60. Found: C, 46.49; H, 4.86; Br, 34.40.

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Registry No.—**4**, 68867-09-4; **4** anion, 68867-13-0; **5**, 68867-10-7; **6**, 68867-11-8; 2-cyclopentylacetaldehyde, 5623-81-4; cyclopentylethanol, 766-00-7; glyoxylic acid, 298-12-4; 3-cyclopentyl-4-hydroxy-2-butenolide, 68867-12-9; cyclopentyl bromide, 137-43-9.

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Selective Reduction of Mono- and Disubstituted Olefins by Sodium Borohydride and Cobalt(II)

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Application of transition metal hydrides in organic synthesis has attracted increasing attention in recent years.[1] Although the complexed reagents, presumably transition metal hydrides, prepared from transition metal salts, e.g., Fe(II), Ti(IV), Zr(IV), etc., and metal hydrides, e.g., $LiAlH_4$ and NaH, have been reported to reduce alkenes and alkynes,[2] $NaBH_4$ has not been used extensively in the preparation of such complexed reducing reagents.[3] We now wish to report our observation that the complex species prepared from Co(II) salt and $NaBH_4$ reduced alkenes and alkynes in high yields, and that this reagent displays an extremely high steric selectivity in the reduction of alkenes.[4]

As shown in Table I, monosubstituted terminal olefins (entries 1–3) are most easily reduced by this reagent, the reactions being complete in 1 h. Disubstituted olefins (entries 4–10) are in general more slowly reduced, although reduction of norbornene and norbornadiene is exceptionally facile. It is also noteworthy that the reduction rates are significantly different for *cis*- and *trans*-stilbenes, with the cis isomer being more easily reduced (entries 7 and 8). While mono- and disubstituted olefins are efficiently reduced by this reagent, the more highly substituted olefins (entries 11–15) are virtually inert to these reducing conditions. The potential synthetic utility of this reducing agent is well demonstrated in the reduction of limonene (entry 9), in which the disubstituted side-chain olefin is selectively reduced in the presence of the trisubstituted endocyclic double bond. The observed selectivity in the reduction (mono- > di- > tri- and tetrasubstituted) can be best explained in terms of steric effects, although the involvement of the electronic effect to a minor degree cannot be excluded.

Alkynes are also facilely reduced to alkanes (entries 16–18). Although the partial reduction of alkyne to alkene could be easily achieved by limiting the amount of $NaBH_4$ in the case of 1-octyne (entries 16 and 17), apparently this is not general (entry 18).[5]

Alcoholic $NaBH_4$ was reported to react with Co(II) to produce, depending on the reaction conditions, Co metal, $Co(BH_4)_2$, or complexed cobalt hydrides.[6] It is reasonable to assume that the species responsible for the selective reduction of alkenes and alkynes is most likely a cobalt hydride. The isotope labeling results in the reduction of 1-dodecene (Table II) seem to support this assumption. The results can be best accommodated by the following mechanistic picture. The reaction of Co(II) and $NaBH_4$ produces a cobalt hydride species which is capable of exchanging H ligands with the medium or hydrated water (see the difference of d_0 between entries 1–3). The reduction of the olefin presumably involves the initial hydrocobaltation followed by reductive cleavage

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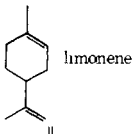
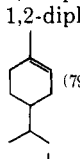
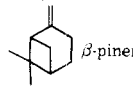
Table I. Reduction of Alkenes and Alkynes by $NaBH_4$ and Co(II)[a]

entry	substrate	registry no.	produce (% yield)	mol ratios of substrate/ Co(II)/$NaBH_4$	reaction time, h	$T_{1/2}$
1	styrene	100-42-5	ethylbenzene (>98)[b]	1/1/2	3.5	<10 min
2	1-octene	111-66-0	*n*-octane (>98)[b,d]	1/1/2	3	<10 min
3	1-dodecene	112-41-4	*n*-dodecane (95)[c,d]	1/1/2	3	
4	norbornene	498-66-8	norbornane (>98)[b]	1/1/2	3	
5	norbornadiene	121-46-0	norbornane (>98)[b]	1/1/2	2.5	
6	cyclohexene	110-83-8	cyclohexane (>98)[b]	1/1/2	20	~2 h
7	*cis*-stilbene	645-49-8	1,2-diphenylethane (>98)[b]	1/1/2.5	16	<2 h
8	*trans*-stilbene	103-30-0	1,2-diphenylethane (45)[b]	1/1/2.5	16	~20 h
9	 limonene	138-86-3	 (79)[c]	1/0.5/1	12.5	~6 h
10	 β-pinene	127-91-3	 (44)[c]	1/0.5/1	20	
11	1-methylcyclohexene	591-49-1	no reaction	1/1/3	19	
12	α-pinene	80-56-8	no reaction	1/1/2	24	
13	cholesterol	57-88-5	no reaction	1/1/2	23	
14	cholesteryl acetate	604-35-3	no reaction	1/1/2	24	
15	lanosterol	79-63-0	no reaction	1/1/2	24	
16	1-octyne	629-05-0	*n*-octane (>98)[b]	1/0.1/1	3	
17	1-octyne		1-octene (>95)[b]		3	
			n-octane (trace)	1/0.1/0.5		
			1-octyne (trace)			
18	1,2-diphenylacetylene	501-65-5	*cis*-stilbene (30)[b,c]	1/0.1/0.5	11	
			trans-stilbene (10)			
			1,2-diphenylethane (10)			
			1,2-diphenylacetylene (50)			
19	cyclohexanone	108-94-1	cyclohexanone (~30)	1/1/2	10	
			cyclohexanol (~70)			

[a] All the reactions were run in EtOH (see text). [b] Determined by VPC. [c] Determined by NMR. [d] $CoCl_2 \cdot 6H_2O$ and anhydrous $CoBr_2$ could be used interchangeably.

Table II. Isotope Labeling Study with 1-Dodecene[a]

entry	reaction conditions	$d_0/d_1/d_2/d_3/d_4/d_5$[b]
1	$CoCl_2 \cdot 6H_2O$–$NaBD_4$–EtOH	3.8/6.9/6.1/2.4/0.8/0.2
2	$CoBr_2$–$NaBD_4$–EtOH	3.3/7.0/6.9/2.6/1.0/0.3
3	$CoBr_2$–$NaBD_4$–EtOD	1.4/4.2/5.7/3.0/1.2/0.3

[a] Molecular ion ratios were determined at 15 eV on a Hewlett-Packard GC–mass data system 5982-A. [b] Relative abundances of molecular ions based on the base peak at *m/e* 57 and corrected for the amount of natural abundance of M + 1.

of the C–Co bond. The multiple (higher than d_2) deuterium label incorporation indicates that the hydrocobaltation is reversible. Since the regiospecific and reversible addition of H–CoLn to the olefin can only account for the incorporation of up to three or four deuteriums, the incorporation of up to d_5 suggests that the hydrocobaltation process may be nonregiospecific. The observation that both the *cis*- and *trans*-stilbene isomers are obtained in the reduction of 1,2-diphenylacetylene should also have interesting mechanistic implications concerning the properties and reductive cleavage of the C–Co bond.

The reduction of alkenes and alkynes by $NaBH_4$ and Co(II) should prove to be of considerable synthetic value due to its high selectivity and its operational simplicity.

Experimental Section

All the products were identified by comparison with readily available authentic samples. Melting points were taken on a Reichert Hot Stage M.P. apparatus. The NMR spectra were obtained on Varian Asosciates Model T-60 with Me_4Si as internal standard. Mass spectral analyses were done on a Hewlett-Packard GC–MS system 5982-A. VPC analyses were performed with Antek Instrument Model 300 and Varian Aerograph Model 2700 by using the following columns; 5 ft of 10% OV-101 and 5 ft of 10% FFAP on Anakrom-SD, 60/70 mesh.

General Procedure of Reduction. To a solution of 1-dodecene (1.68 g, 10 mol) and $CoCl_2 \cdot 6H_2O$ (2.38 g, 10 mmol) in ethanol (25 mL) under Ar at 0 °C was added $NaBH_4$ (760 mg, 20 mmol) in portions. The solution immediately became dark with evolution of hydrogen. The mixture was stirred under Ar at room temperature for 3 h and poured into a 3 N HCl solution. The aqueous solution was extracted with ether. The ether layer was washed (H_2O), dried ($MgSO_4$), and evaporated to give the product.[7] It was found that up to 50% of DME, THF, and ether could be used as cosolvent with ethanol, although the reduction appeared sluggish in these solvents alone. Substituting $CoCl_2 \cdot 6H_2O$ for anhydrous $CoBr_2$ did not have any noticeable effect on the reduction.

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Registry No.—Sodium borohydride, 16940-66-2; cobalt(II) chloride hexahydrate, 7791-13-1; cobalt(II) bromide, 7789-43-7.

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An Efficient and Convenient Synthesis of Fluoroformates and Carbamoyl Fluorides

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Methods for the preparation of enol carbonates, $R_2C{=}C\text{-}ROCO_2R$ (**1**), and enol carbamates, $R_2C{=}CROCONR_2$ (**2**), have been reported[1,2] and some of the advantages of these synthetic intermediates have been outlined[2] in recent publications from this laboratory. In our search for other broadly useful and complementary routes to **1** and **2**, we have now developed[3] a simple, regiospecific preparation from enol silyl ethers and fluoroformates, ROCOF (**3**), or tertiary carbamoyl fluorides, R_2NCOF (**4**).

The success of this new procedure requires that **3** and **4** be readily available and here the literature is discouraging. Both **3** and **4** have been made in high yield by acylation of alcohols or amines with COF_2 or COFCl,[4] but the method is economically impractical because of the price of commercial COF_2 ($700 per lb) and the preparative inaccessibility of both COF_2 and COFCl in a standard laboratory.[5] Chloroformates also have been converted to **3** but the yields are only moderate and the halogen exchange process requires special apparatus (e.g., UV light with KF[6]) or reagents (e.g., freshly prepared thallous fluoride[7]).[8] More complex fluoroformate syntheses also have been described.[9]

We have now found that the conversion of chloroformates (**5**) and carbamoyl chlorides (**6**) to **3** and **4**, respectively, is easily achieved in excellent yield just by treatment with KF activated by the phase transfer agent, 18-crown-6.[10] The results for several syntheses are summarized in Table I. For liquids **5** and **6** (often commercially available), it is merely sufficient to stir the neat starting material with KF and a little 18-crown-6 (ca. 5 mol %) at room temperature until none of the carbonyl chloride remains (IR assay).[11] The pure product is then simply isolated by distillation of the reaction mixture. When the reactant is a solid, an inert solvent such as dichloromethane is used to facilitate the process.

That the halogen exchange, **5** → **3**, can be performed as described above may be somewhat surprising since the analogous transformation of **5** to a cyanoformate with 18-crown-6 activated KCN reported by Childs and Weber is extremely sluggish in the absence of a little water[12]—a contaminant which would destroy the product in the present reaction. In the only other close precedent for the present work, Liotta and Harris[13] showed that acetyl fluoride could be generated from acetyl chloride with crown ether activated KF. However, that process may be complicated by the equilibrium intermediacy of an anion-hungry *N*-acetylacetonitrilium cation and also is not a practical route to pure acetyl fluoride. Even careful fractional distillation yields a product contaminated by ca. 20% acetonitrile. By our procedure (see Table I), both butyryl fluoride[14] and benzoyl fluoride[8] were obtained pure in 90% yield from the corresponding chlorides.

From Table I, a large variation in required reaction time vs. substrate structure is evident. At a given temperature and catalyst concentration, the smaller molecules generally exchange halogen faster in accord with expectation: shorter alkyl residues on the carbonyl chloride increase its polarity as a solvent thus increasing the solution concentration of the other reactant, the polar KF crown ether complex. The concentration of complex also can be raised by using more crown ether, a simple way to speed up those reactions which are slower than desired.

Raising the temperature is another way to accelerate the exchange. However, this mechanism must be used with caution here. Alkyl chloroformates are known to decompose to alkyl chlorides or alkenes and CO_2 when heated[15] (usually at 120–150 °C or higher) and this process seems to be strongly catalyzed by both KF and 18-crown-6 at elevated temperatures. For example, *i*-BuOCOF (**7**) was isolated in 91% yield when the chloroformate was allowed to react at room temperature. At 100 °C the yield of **7** was only 35% and much isobutyl chloride also was found. The result cannot be accommodated by invoking product decomposition, since **7** was reasonably stable under these conditions. However, when *i*-

Table I. Fluoroformates, Carbamoyl Fluorides, and Acyl Fluorides Prepared from Their Respective Chlorides[a]

RCOF product, R =	registry no.	yield,[b] %	KF, equiv	18-C-6, mol %	temp, °C	time, h	bp, °C/torr found	bp, °C/torr lit.[c]
$MeCH_2O$–	461-64-3	89	1.6	6	0	68	55–57/atm	57/atm[4a]
Me_2CHO–	461-71-2	95	1.6	6	13	47	66–70/atm	81–82/atm[7]
Me_2CHCH_2O–	53813-78-8	91	1.3	4	r.t.	45	92–93/atm	27/0.1[9a]
$MeCH_2CH_2CH_2O$–	2253-35-2	84	1.8	8	r.t.	73	99–100/atm	97–99/atm[4b]
c-$C_6H_{11}O$—	351-79-1	89	1.5	9	70	4	52–53/21	64–65/25[7]
cholesteryl-3-O[d]	65928-85-0	89	3.9	15	r.t.	53	mp 112–113[e]	
PhO–	351-80-4	80	1.6	6	15–19	144	60–64/120	153/atm[4a]
Me_2N–	431-14-1	95	1.3	4	r.t.	27	65–70/80	54–56/51[5b]
N-piperidino–	657-99-8	88	1.9	5	r.t.	31	75–77/10[f]	61/11[9b]
N-morpholino–	68928-13-2	97	2.9	6	r.t.	68	60–65/2[g]	
$MeCH_2CH_2$–	461-53-0	90	1.4	4	r.t.	27	66–67/atm	69/atm[14]
phenyl–	455-32-3	90	2.1	7	r.t.	234	56–57/20	159–161/atm[8]

[a] Made by the general procedure in the Experimental Section with variations indicated in the table. [b] Of distilled or recrystallized product. [c] Superscripts refer to reference numbers in the text. [d] Prepared from the solid chloroformate in CH_2Cl_2; see text. [e] New compound; converted to and compared with known cholesteryl vinyl carbonate.[2c] [f] Converted to and compared with known *N*-vinyloxycarbonylpiperidine.[2b] [g] New compound; converted to and compared with the known enol carbamate of methyl vinyl ketone.[3]

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