597-49-9; phenol, 108-95-2; 2,6-di-*tert*-butylphenol, 128-39-2; *n*-hexylamine, 111-26-2; 1-hexanethiol, 111-31-9; benzenethiol, 108-98-5; *n*-hexanol, 66-25-1; benzaldehyde, 100-52-7; 2-heptanone, 110-43-0; norcamphor, 497-38-1; acetophenone, 98-86-2; benzophenone, 119-61-9; cinnamaldehyde, 104-55-2; 3-penten-2-one, 625-33-2; 2-cyclohexenone, 930-68-7; chalcone, 94-41-7; cinnamyl alcohol, 104-54-1; cyclohexanol, 108-93-0; 1,3-diphenyl-2-propen-1-ol, 4663-33-6; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 3,3,5-trimethylcyclohexanone, 873-94-9; 4-*tert*-butylcyclohexanone, 98-53-3; *d*-camphor, 464-49-3; *cis*-2-methylcyclohexan-1-ol, 7443-70-1; *trans*-3-methylcyclohexan-1-ol, 7443-55-2; *cis*-4-methylcyclohexan-1-ol, 7731-28-4; *trans*-3,3,5-trimethylcyclohexan-1-ol, 767-54-4; *cis*-4-*tert*-butylcyclohexan-1-ol, 98-52-2; *endo*-norcamphor-2-ol, 497-36-9; (1*R*)-*exo*-camphor-2-ol, 10334-13-1; *p*-benzoquinone, 106-51-4; anthraquinone, 84-65-1; hexanoic acid, 142-62-1; benzoic acid, 65-85-0; acetic anhydride, 108-24-7; succinic anhydride, 108-30-5; phthalic anhydride, 85-44-9; hexanoyl chloride, 142-61-0; benzoyl chloride, 98-88-4; ethyl hexanoate, 123-66-0; ethyl benzoate, 93-89-0; phenyl acetate, 122-79-2; γ-butyrolactone, 96-48-0; phthalide, 87-41-2; isopropenyl acetate, 108-22-5; 1-butene oxide, 106-88-7; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; *trans*-2-butene oxide, 21490-63-1; 2-methyl-2-butene oxide, 5076-19-7; 1-methylcyclohexene oxide, 1713-33-3; 2,3-dimethyl-2-butene oxide, 5076-20-0; 2-butanol, 78-92-2; 1-phenylethanol, 98-85-1; 3-methyl-2-butanol, 598-75-4; 2-methyl-2-butanol, 75-85-4; 1-methylcyclohexanol, 590-67-0; hexanamide, 628-02-4; benzamide, 55-21-0; *N,N*-dimethylhexanamide, 5830-30-8; *N,N*-dimethylbenzamide, 611-74-5; hexanenitrile, 628-73-9; benzonitrile, 100-47-0; 1-nitropropane, 108-03-2; nitrobenzene, 98-95-3; azobenzene, 103-33-3; azoxybenzene, 495-48-7; cyclohexanone oxime, 100-64-1; phenyl isocyanate, 103-71-9; pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7; 1-chlorooctane, 111-85-3; 1-bromooctane, 111-83-1; 1-iodooctane, 629-27-6; 2-bromooctane, 557-35-7; cyclohexyl bromide, 108-85-0; *N*-octyl tosylate, 3386-35-4; cyclohexyl tosylate, 953-91-3; di-*n*-butyl disulfide, 629-45-8; dipheny disulfide, 882-33-7; methyl *p*-tolyl sulfide, 623-13-2; dimethyl sulfoxide, 67-68-5; diphenyl sulfone, 127-63-9; *p*-toluenesulfonic acid, 104-15-4; triphenylborane, 960-71-4.

Molybdenum(0)-Catalyzed Reductive Dehalogenation of α-Halo Ketones with Phenylsilane

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Reductive dehalogenation of α-halo ketones and esters is effectively achieved by using a novel reducing system comprised of phenylsilane and catalytic amounts of molybdenum hexacarbonyl and triphenylphosphine. Reactions are carried out at 60–80 °C in variety of solvents, including THF, benzene, toluene, and diglyme. With respect to α-halo carbonyl reduction, this combination of Mo(0) and phenylsilane is superior to our previously described palladium(0)/diphenylsilane system and produces higher yields and cleaner products.

Introduction

Methods for selective removal of halogen substituents adjacent to a carbonyl functionality yielding the parent carbonyl compound have recently received considerable attention. The various procedures and reagents that have been developed for reductive dehalogenation of α-halo carbonyl compounds include (a) reducing agents such as zinc in acetic acid,[1] sodium dithionate,[2] organotin hydrides,[3] borohydride,[4] and low-valent transition-metal salts (e.g. titanium(III),[5] vanadium(II),[6] and chromium(II)[7]); (b) strong nucleophiles that may act as reducing agents such as iodide ions,[8] phosphines,[9] iodophosphines,[10] iodotrimethylsilane,[11] thiols,[12] selenols,[13] tellurolates,[14] amines[15]; (c) stoichiometric amounts of zero-valent transition-metal carbonyls of iron,[16] cobalt,[17] and molybdenum[18]; and (d) heterogeneous hydrogenation catalysts involving transition-metal surfaces.[19]

In recent years we have developed an array of composite reducing systems based on new combinations of tin or silicon hydrides with transition-metal catalysts, including palladium,[20] ruthenium,[21] and molybdenum.[22] These represent a promising new family of reducing media, particularly useful for reductive cleavage of allylic heter-

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Table I. Reduction of α-Halo Ketones with Pd(0)/Ph_2SiH_2[a]

entry	substrate (mmol)	$Pd(PPh_3)_4$ (mol %)	Ph_2SiH_2 (equiv)	additive (equiv)	solvent	temp	time (h)	yield[b] (%)
1	**3**, 0.59	7	1.3	$ZnCl_2$ (2.8)	$CHCl_3$	RT[f]	1	70
2	**3**, 0.83	8	1.5		THF	RT	0.5	73
3	**3**, 0.83	8	1.5[c]		THF	RT	20	5
4	**3**, 0.83	8	1.5[d]		THF	RT	0.1	60
5	**3**, 0.30	8[e]	1.4	PPh_3 (0.16)	THF	RT	24	70
6	**2**, 0.32	7	1.1	$ZnCl_2$ (0.33)	THF	RT	12	50
7	**2**, 0.32	7	1.1		THF	RT	12	60
8	**2**, 0.54	3.5	0.9	NaOAc (1.6)	THF	RT	4	60
9	**2**, 0.32	7	1.1	K_2CO_3 (1)	THF	RT	6	70
10	**7**, 0.19	10	3	K_2CO_3 (1.8)	THF	RT	12	55
11	**9**, 0.37	5	2.2	K_2CO_3 (2)	THF	RT	12	25

[a] All reactions were carried out according to the general procedure given in the Experimental Section. [b] Yields were determined by GC and/or by NMR using internal standards. [c] Et_3SiH was used instead of Ph_2SiH_2. [d] $PhSiH_3$ was used instead of Ph_2SiH_2. [e] $Pd(OAc)_2$ was employed instead of $Pd(PPh_3)_4$. [f] RT = room temperature.

Table II. Mo(0)-Catalyzed Reduction of 3-Bromoheptan-4-one[a]

entry	substrate (mmol)	$Mo(CO)_6$ (mol %)	$PhSiH_3$ (mol %)	PPh_3 (mol %)	$NaHCO_3$ (mol %)	solvent (mL)	temp (°C)	time (h)	yield[b] (%)
1	0.13	25			110	THF (1.0)	65	3.0	traces
2	0.30	2.3	170			THF (1.0)	65	2.0	18
3	0.18	6.4	240			THF (1.0)	65	2.0	33
4	0.20	20	200			THF (1.0)	65	4.0	75
5	0.17	49	180			THF (1.0)	65	2.5	100
6	0.17	23	230		260	THF (0.5)	65	1.75	100
7	0.23	3.3	170				70	0.5	15
8	0.30	4.7	200		130		70	1.0	24
9	0.35	11	170				80	0.5	50
10	0.12	4.4[c]	160			THF (1.0)	65	4.0	no reaction
11	0.34	5	150	17	100	THF (1.0)	65	2.25	100
12	0.34	6	150	23	110	benzene (1.0)	80	2.75	97
13	0.25	7	200	27	130	hexane (0.5)	80	3.0	no reaction
14	0.31	7.4	190[d]	30.3	100	THF (1.0)	65	12	100
15	0.34	7.5	240[e]	29.1	120	THF (1.0)	65	3.5	6
16	0.33	5.7	150	24.7	230	THF (1.0)	65	0.8	100
17	0.44	5.5	40	24.5	180	THF (1.0)	65	2.3	79
18	0.33	40	20		190	THF (1.0)	65	2.0	45

[a] All reactions were carried out according to the general procedure given in the Experimental Section. [b] Yields were determined by GC and/or by NMR by using internal standards. [c] $Mo(N_2)_2(dppe)_2$ was employed instead of 1. [d] Ph_2SiH_2 was employed instead of phenylsilane. [e] Polymethylhydrosiloxane (PMHS) was employed instead of phenylsilane.

osubstituents under extremely mild conditions and for highly controlled conjugate reduction of α,β-unsaturated carbonyl compounds.

In this paper we describe a new application of such composite reducing systems for reductive dehalogenation of α-halo carbonyl compounds.

Results and Discussion

One might anticipate that the α-halo carbonyl functionality, being isoelectronic with the allylic halide function, would be easily reduced to the parent carbonyl by a system that reduces allylic functions. This hypothesis was also supported by the report that reductive dehalogenation of α-halo ketones takes place with the Pd(0)/hexamethyldisilane system,[23] although under drastic conditions (i.e. 140–170 °C for 4–17 h). Indeed, our initial attempts to reduce phenacyl bromide (**3**) with Pd(0)/Ph_2SiH_2, using the optimal conditions that we used earlier for allylic reduction,[20d] resulted in formation of acetophenone within less than 1 h. yields, however, did not exceed 70–80% (Table I, entries 1–4). Monohydridosilanes

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Table III. Mo(0)-Catalyzed Reduction of α-Halo Carbonyl Compounds[a]

entry	substrate (mmol)	$Mo(CO)_6$ (mol %)	$PhSiH_3$ (mol %)	PPh_3 (mol %)	$NaHCO_3$ (mol %)	solvent (mL)	temp (°C)	time (h)	yield[b] (%)
1	**3** (0.21)	6	240	26	250	THF (0.75)	65	5.0	90
2	**3** (0.62)	6	120	27	110	benzene (1.00)	80	3.25	95
3	**4** (0.24)	5	210	20	150	THF (0.75)	65	4.5	100
4	**4** (0.50)	8	150	33	130	benzene (1.00)	80	2.0	>95
5	**4** (0.25)	5	200	19	140	toluene (0.50)	95	1.0	>95
6	**5** (0.41)	5	180	19	80	THF (0.75)	65	1.0	>95
7	**5** (0.41)	6	180	26	80	benzene (0.50)	80	1.0	77
8	**6** (0.30)	5	200	23	100	THF (0.75)	65	1.33	80
9	**7** (0.31)	7	190	26	140	THF (1.00)	65	8.5	35
10	**7** (0.21)	6	280	24	130	toluene (0.50)	75	12.0	45
11	**7** (0.44)	11	160			THF (1.5)	65	2.5	100
12	**8** (0.42)	7	130	26	150	THF (1.00)	65	8.75	70
13	**8** (0.45)	6	160	26	80	toluene (0.50)	75	5.5	90
14	**9** (0.39)	5	160	19	110	benzene (0.50)	80	2.5	70
15	**10** (0.29)	7	170	31	120	THF (0.75)	65	2.0	>95
16	**10** (0.38)	4	160	16	80	diglyme (0.50)	75	1.2	100
17	**11** (0.40)	6	150	20	80	THF (1.00)	65	1.0	100
18	**12** (0.32)	5	190	17	100	THF (0.75)	65	5.5	100
19	**13** (0.49)	4	140	18	70	THF (0.75)	65	4.5	90
20	**14** (0.40)	6	170	26	110	benzene (0.50)	80	24	75

[a] All reactions were carried out according to the general procedure given in the Experimental Section. [b] Yields were determined by GC and/or by NMR by using internal standards.

such as triethylsilane or polymethylhydrosiloxane were found to be essentially inert in this reaction. Conversely, phenylsilane was too reacive, reminiscent of the behavior of tributyltin hydride,[20e] its palladium-catalyzed decomposition into disilane and hydrogen gas occurring at a rate that is either comparable to or greater than that of reduction.

Although reduction proceeded quite rapidly, formation of the parent ketone was accompanied by substantial quantities of unidentified polar side products. This drawback became even more significant with more sterically hindered substrates, their reduction proceeding much more sluggishly. For example, reduction of 3-bromoheptan-4-one (**2**) was approximately ten times slower than that of **3** and gave only moderate yields (Table I, entries 6–9). Addition of $ZnCl_2$ (which is known to promote Pd(0)-catalyzed reductions[20a–d]) had no effect on either reaction rate or yield. Using a slightly basic medium, however, engendered by addition of potassium carbonate, produced somewhat higher reduction rates and yields, but these conditions also promoted formation of the corresponding α,β-unsaturated ketone, possibly via a β-hydride elimination process of the corresponding palladium enolate.[24] Reduction of a more sterically hindered secondary bromo ketone, bromocamphor (entry 10), proceeded, as expected, with lower efficiency. Much lower yields were observed in the case of tertiary bromo ketone **9** (entry 11).

The rather poor results obtained with palladium(0) turned our attention to molybdenum(0), which in addition to its catalytic potential is an effective reducing agent by virtue of its stable high oxidation states.[25] In fact, $Mo(CO)_6$ (**1**) is one of the few soluble transition-metal complexes that were found active in reductive dehalogenation of α-halo ketones,[16–18] stoichiometric quantities of which were employed for this purpose by Alper.[18]

Table II summarizes our initial studies with **1**. We have chosen 3-bromoheptan-4-one (**2**) as our model substrate because both **2** and its reduced form, 4-heptanone, can be easily, quantitatively determined by either GC or ^1H NMR. Alper's homogeneous reaction conditions involve heating the substrate to 85–90 °C for 48 h with equimolar amounts of **1** in dry DME.[18] Therefore, as expected, our initial attempts to reduce **2** with catalytic amounts of **1** in refluxing THF for less than 3 h at 65 °C resulted in only negligible traces of 4-heptanone[26] along with substantial amounts of unidentified side products (Table II, entry 1).

The situation was significantly improved by adding hydridosilane to the system. As illustrated in Table II, entries 2–6, this modification enabled complete reduction of **2** with less than equimolar quantities of **1**. Yet, it appears that even in the presence of excess phenylsilane, 1 mol of **1** cannot reduce more than 5 mol of **2**. This stoichiometry cannot be regarded as a catalytic process because Mo may be easily oxidized up to the +5 and even +6 oxidation states. Increasing temperature, addition of sodium bicarbonate, or carrying out the reaction in the absence of solvent all resulted in only minor improvements of reduction rates and yields (entries 7–9) but did not increase the molybdenum turnover numbers beyond five.

Assuming that the problem arises from the difficulty of regenerating Mo(0) from its partially oxidized forms, we looked for methods to stabilize the catalyst. One approach involved the employment of $Mo(N_2)_2(dppe)_2$, which is a useful catalyst in a number of transfer hydrogenation reactions.[27] This complex, however, was found to be ineffective for our reaction (Table II, entry 10). Nevertheless, addition of triphenylphosphine to **1** (about 3–4 equiv of PPh_3 per molybdenum) resulted in a truly catalytic process involving molybdenum, allowing employment of less than 2 mol % of this transition metal. Interestingly, higher concentrations of phosphine ligands did not inhibit the reaction. In fact, any concentration ratio of PPh_3 to Mo(0) from 2:1 to 20:1 had equal effects on reaction rates and

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(26) It appears that rapid reduction occurs at elevated temperatures. Injecting a sample of the reaction mixture (containing **2** and at least 20 mol % of **1** with or without silane) to the GC injection port (>250 °C) resulted in an apparent quantitative conversion into 4-heptanone. This observation, however, does not represent the situation in benzene or THF at reflux temperatures. Essentially no reaction was observed when the molybdenum complex was removed from the mixture (by precipitation with cold hexane and filtration) prior to injection into the GC. Accordingly, no reaction was observed when the mixture was analyzed by NMR instead of GC.

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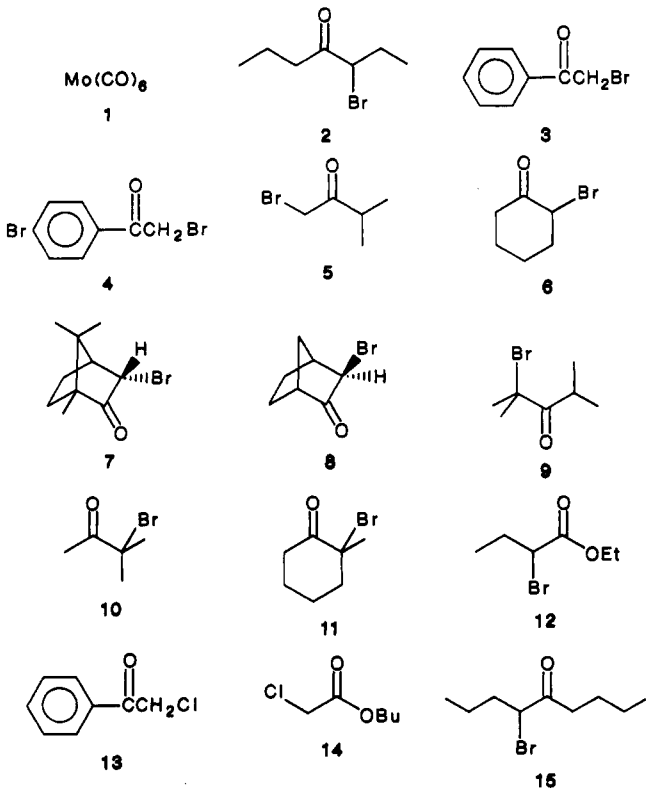
Chart I



yields. An exception to this generalization is the reduction of bromocamphor, **7** (entries 9–11 in Table III), in which the absence of phosphine ligands resulted in a truly catalytic reaction and significantly higher yields.

Reactions proceeded with satisfactory rates in either refluxing THF or benzene or in toluene and diglyme at similar temperatures, but not, however, in hexane, which is a poor solvent for the molybdenum complex (Table II, entries 11–13, and Table III). Using GC analyses, no change in reduction rates was observed on addition of a solid base (e.g. $NaHCO_3$). However, in the absence of base, the reaction mixture turned highly acidic, causing deterioration of both starting material and product and increasing the amounts of side products, particularly during long reactions.

In agreement with our previous work on conjugate reductions with the Mo(0)/silane system,[22] $PhSiH_3$ was found to be the most reactive hydridosilane out of a dozen readily available hydridosilanes checked.[20c] For example, reduction with diphenylsilane (Table II, entry 14) proceeded between 10 to 20 times slower than that with phenylsilane, and the corresponding reaction with polymethylhydrosiloxane (PMHS) was found to be too slow to be practial (Table II, entry 15). It appears that the required amount of phenylsilane for complete reduction is approximately 0.5 mol per mol of substrate, implying that two out of the three hydrides of the silane molecule may actively participate in the reaction (Table II, entries 16–18). Nevertheless, in order to achieve maximal reduction rates, particularly on a small scale, we employed more than 1 mol of hydridosilane per mol of substrate.

Thus, the set of conditions described in entry 16 of Table II represents a satisfactory system for reduction of **2**, leading to quantitative reduction in less than 50 min. Using this optimal set of conditions, reduction of a dozen other α-halocarbonyl compounds (Chart I) was carried out successfully, demonstrating the generality of this reaction (Table III).

From the examples in Table III, it appears that the reaction proceeds equally well with primary, secondary, and tertiary bromo ketones. α-Chloro carbonyl compounds may also be reduced under these conditions, and the reaction is applicable to ketones as well as to esters. aromatic bromide (Table III, entries 3 and 4) remains intact under the reaction conditions.

Although most of the reactions described in Table III were carried out on a small scale, reductions may be conveniently performed on a preparative scale. For example, reduction of 1.62 g of bromononanone **15** was completed within 80 min, affording 5-nonanone in 96% yield. Similarly, conversion of α-bromocamphor (**7**) into camphor (81%) was carried out on a 10-mmol scale.

At this point the exact details of the catalytic cycles of both the palladium-and molybdenum-catalyzed reductions are unknown. It is conceivable that in both cases the reaction involves an oxidative addition of the halo carbonyl to the transition metal, leading to the corresponding palladium or molybdenum enolate, followed by hydride transfer to the metal, and subsequently to the substrate. This assumption is supported in the Pd case by the appearance of substantial quantities of the corresponding α,β-unsaturated ketone.[24] Also, reduction of phenacyl bromide with dideuteriodiphenylsilane and Pd(0) catalyst resulted in formation of monodeuterioacetophenone as the major product (proved by GCMS analysis). Similar deuterium incorporation was observed with molybdenum as well when reduction of **9** and **10** was carried out with phenyltrideuteriosilane. Nevertheless, the molybdenum case seems to differ from that of palladium, as reduction also proceeds to some extent in the absence of silane. However, the difference in reaction rates observed with or without silane indicates that the actual catalyst is, probably, an activated molybdenum complex, generated by reaction of **1** and hydridosilane. The existence of such an activated catalyst is supported by the observation of a latent period of 0.2–2 h in most of the reactions. In some cases, the reduction itself was shorter than the latent period. Moreover, addition of a working reaction mixture to a fresh one resulted in rapid reduction of the additional substrate with no latent period. It appears that both activation of the catalyst and the reduction itself require temperatures of at least 60–70 °C, as no reaction took place at room temperature by using a heat-treated THF solution of **1** and phenylsilane.

Conclusion

This study has demonstrated the advantages of using phenylsilane with catalytic amounts of molybdenum hexacarbonyl and triphenylphosphine as an effective reducing system for reductive dehalogenation of α-halo carbonyl compounds. With respect to α-halo carbonyl reduction, this Mo(0) system was found to be superior to our previously described palladium(0)/diphenylsilane mixture, resulting in higher yields and clean products.

Experimental Section

Infrared spectra were measured on the neat compounds on a FT/infrared Nicolet MX-1 spectrometer. ^1H NMR spectra were measured in deuteriochloroform of a Varian FT-80A or Bruker WH-270 NMR spectrometer. GC-MS analyses were carried out on a Finnigan 4500 spectrometer. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F-254, Art. No. 5549). Column chromatography separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh, Ar. No. 9385) under pressure of 0.4 atm (flash chromatography). GC analyses were performed on a Spectra Physics 7100 (FI detector) gas chromatograph equipped with a 0.125 in. × 2 ft column packed with 10% SE-30 on

Chromosorb W. Preparative GC separations were carried out with a Varian Aerograph 90P (TC detector) equipped with either a $^1/_2$ in. × 20 ft column packed with 10% carbowax 20M on Chromosorb W or a $^3/_8$ in. × 20 ft column packed with 10% SE-30 on Chromosorb W. Distillations were usually performed with a Buchi Kugelrohr apparatus and the temperatures given are pot temperatures. Tetrahydrofuran, diglyme, benzene, and toluene were distilled over sodium benzophenone ketyl. Tetrakis(triphenylphosphine)palladium was prepared from palladium dichloride.[28] Phenylsilane and phenyltrideuteriosilane were prepared by reduction of trichlorophenylsilane with $LiAlH_4$ and $LiAlD_4$, respectively, in dry ether.[29]

Substrates. Compounds **3**, **4**, **7**, **12**, and **13** were purchased from Aldrich and **14** from Light & Co. Ltd. Compound **5** was prepared as reported.[30] Compounds **2**, **8**,[31] **9**,[32] **10**,[33] and **15** were prepared by dropwise addition of bromine (0.1 mol) into a solution of the parent ketone (0.1 mol) in glacial acetic acid (50 mL) at room temperature, followed by extraction with ether, washing with aqueous sodium carbonate, removal of the solvent, and finally vacuum distillation. All products were found to be pure by GC and NMR. Compounds **6**[34] and **11**[35] were prepared by dropwise addition of bromine (0.1 mol) into a vigorously stirred mixture of the parent ketone (0.1 mol) in water (50 mL) at room temperature, followed by ether extraction and distillation.

General Procedure for Dehalogenation with Pd(0) Catalyst. The α-halo ketone (0.10–0.83 mmol) was dissolved in THF (5 mL) along with diphenylsilane (1.0–3 equiv) and, in some cases, K_2CO_3 (1–2 equiv). $Pd(PPh_3)_4$ (3.5–10 mol %) was added and the mixture was stirred at room temperature (inert atmosphere was not required). The composition of reaction mixture was monitored by GC using internal standards. More details are given in Table I.

General Procedure for Dehalogenation with Mo(0) Catalyst. The α-halo carbonyl substrate (0.2–0.6 mmol) was dissolved in THF (0.5–1.0 mL) and mixed with $Mo(CO)_6$ (4–11 mol %), triphenylphosphine (17–33 mol %), phenylsilane (120–280 mol %), and sodium bicarbonate (80–250 mol %). The mixture was refluxed or heated to the desired temperature (when other solvent was used). Progress of the reaction progress was monitored by GC and/or NMR, using internal standards. More details are given in Tables II and III.

Preparative Procedures. Reduction of 4-Bromononan-5-one. A mixture comprised of 4-bromononan-5-one (1.62 g, 6.87 mmol), $Mo(CO)_6$ (0.09 g, 0.34 mmol), phenylsilane (1.08 g, 10 mmol), triphenylphosphine (0.35 g, 1.33 mmol), and $NaHCO_3$ (0.83 g, 9.83 mmol) in 7 mL of THF was refluxed for 80 min (completion of the reaction was evident by GC). The mixture was cooled to room temperature, water (0.15 mL) was added, and the solvent was removed under reduced pressure. Distillation of the residue afforded pure (GC, NMR) 5-nonanone (0.98 g, 96% yield).

Reduction of α-Bromocamphor. A mixture of α-bromocamphor (2.24 g, 9.69 mmol), $Mo(CO)_6$ (0.14 g, 0.53 mmol), phenylsilane (1.30 g, 12 mmol), and $NaHCO_3$ (0.88 g, 10.46 mmol) in 6 mL of THF was refluxed for 1.5 h (completion of the reaction was evident by GC). The solution was worked up as described above, affording pure camphor (GC, NMR) (1.19 g, 81% yield).

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Registry No. **1**, 13939-06-5; **2**, 42330-10-9; **2** (debromo deriv), 123-19-3; **3**, 70-11-1; **3** (debromo deriv), 98-86-2; **4**, 99-73-0; **4** (debromo deriv), 99-90-1; **5**, 19967-55-6; **5** (debromo deriv), 563-80-4; **6**, 822-85-5; **6** (debromo deriv), 108-94-1; **7**, 1925-58-2; **7** (debromo deriv), 76-22-2; **8**, 1073-25-2; **8** (debromo deriv), 497-38-1; **9**, 3212-63-3; **9** (debromo deriv), 565-80-0; **10**, 2648-71-7; **11**, 10409-47-9; **11** (debromo deriv), 583-60-8; **12**, 533-68-6; **12** (debromo deriv), 105-54-4; **13**, 532-27-4; **14**, 107-59-5; **14** (debromo deriv), 123-86-4; **15**, 42330-11-0; **15** (debromo deriv), 502-56-7; Ph_2SiH_2, 775-12-2; $Pd(PPh_3)_4$, 14221-01-3; Et_3SiH, 617-86-7; $PhSiH_3$, 694-53-1; $Pd(OAc)_2$, 3375-31-3.

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Fjord Region 3,4-Diol 1,2-Epoxides and Other Derivatives in the 1,2,3,4- and 5,6,7,8-Benzo Rings of the Carcinogen Benzo[*g*]chrysene

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Dihydrodiol and diol epoxide derivatives of the carcinogen benzo[*g*]chrysene (BgCh) have been prepared to probe structural factors involved in the carcinogenesis and mutagenesis of polycyclic aromatic hydrocarbons. Preparation of 1,2-dihydrobenzo[*g*]chrysen-4(3*H*)-one (**6**) and 7,8-dihydrobenzo[*g*]chrysen-5(6*H*)-one (**11**), ketones suitable for further elaboration to potential metabolites of benzo[*g*]chrysene in the 1,2,3,4- and 5,6,7,8-benzo rings, respectively, was achieved through two cyclization steps. Photochemical closure of 2-(1- or 2-naphthyl)styrene derivatives **4** and **9** afforded chrysene and benzo[*c*]phenanthrene ring systems with a butyric ester/acid side chain poised for a second ring closure (acid-catalyzed) to the desired ketones. Preparation of pure BgCh 3,4-diol 1,2-epoxides **23** and **24** from the dihydrodiol diester **14** by conversion to separable trans bromohydrins, cyclization to the epoxides, and hydrolysis of the acetates was found to be more successful than preparation from the dihydrodiol **15**.

In the mid-1970s, evidence linking diol epoxide derivatives of polycyclic aromatic hydrocarbons (PAHs) to the carcinogenicity of PAHs began to emerge.[1,2] Since then, syntheses of these molecules and their dihydrodiol pre-

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