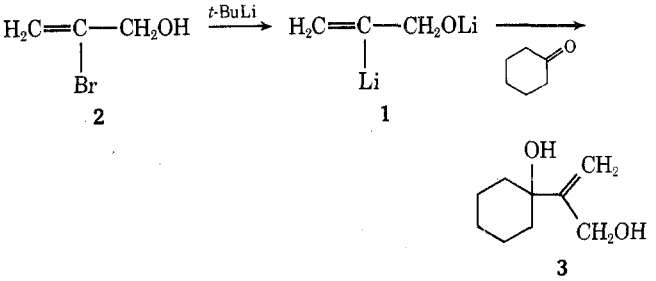
$H_2C{=}C(Li)CH_2N(CH_3)_2$, had been generated and utilized advantageously in earlier work in these laboratories.[2] It was also known that the reaction of metals such as magnesium with ethers of 2-bromoallyl alcohol leads rapidly to allene presumably via the intermediate $H_2C{=}C(Met)CH_2OR$.[3] The generation of 1 has in fact been found to be quite straightforward. Communication of our results at this time has been prompted by the obvious practicality and usefulness of 1 and also by the appearance of a recent paper[4] dealing with two reagents of the same general type (substituted 2-oxido vinyllithium derivatives).

Treatment of the readily available[5] 2-bromoallyl alcohol (2) in ether with 2.5 equiv of *tert*-butyllithium[6] at −78 to 0° resulted in formation of 1 as evidenced by the isolation of the adduct 3 in 73% yield after reaction with cyclohexanone. The unsaturated diols 4 and 5 were similarly obtained from acetone and benzaldehyde in good (65–70%) yield.[7]



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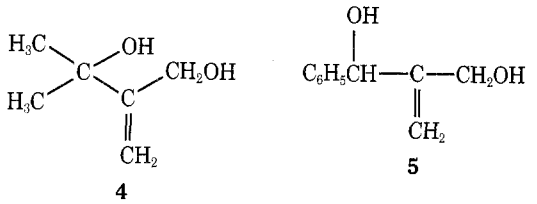

4 5

Experimental Section

General Method. 2-(1′-Hydroxycyclohexyl)allyl Alcohol (3). To a solution of 413 mg (3.01 mmol) of 2-bromoallyl alcohol in 8 ml of ether at −78° was added slowly 7.65 ml of 0.99 *M tert*-butyllithium in pentane. The solution was quickly warmed to 0° and stirred for 4 hr. Cyclohexanone (98.5 μl, 1.0 mmol) was added to the reaction solution and stirring was continued for an additional 1 hr at 0°. The reaction was hydrolyzed with methanol and a minimal amount of water, and the aqueous phase was extracted with ether. The ethereal extracts were combined with the organic phase of the reaction, dried (brine and Na_2SO_4), and concentrated. Preparative TLC (silica gel, 1:1 benzene–ether, R_f 0.25) of the residue gave 113 mg of diol 3 as a clear, colorless oil (73%): ir (film) 3600–3100, 2930, 2855, 1640, 1030, 960, and 905 cm^{-1}; NMR ($CDCl_3$) δ 5.13 (2 H, s, =CH), 4.28 (2 H, s, $-OCH_2$), 3.03 (2 H, br, OH), and 2.1–1.4 (10 H, br s, $-CH_2-$). After recrystallization from hexane–ether, crystalline 3, mp 48.5–50°, was obtained, mass spectrum *m/e* (% of base peak) 156 (4), 138 (19), 95 (64), 81 (64), 67 (90), 55 (100).

Spectroscopic data for 4: ir ($CHCl_3$) 3600–3100, 2970, 1640, 1460, 1375, 1365, 1155, 1010, 915 cm^{-1}; NMR ($CDCl_3$) δ 5.15 (2 H, s, =CH), 4.32 (2 H, s, $-OCH_2-$), 3.47 (2 H, br, OH), 1.60 (6 H, s, $-CH_3$); mass spectrum *m/e* (% of base peak) 101 (69), 83 (39), 59 (100).

Spectroscopic data for 5: ir (film) 3600–3100, 3025, 2870, 1650, 1490, 1450, 1020, 915, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.32 (5 H, s, ArH), 5.25 (1 H, s, ArCHO), 5.15 (2 H, s, =CH), 3.98 (2 H, s, OCH_2), 3.52 (2 H, br, OH); mass spectrum *m/e* (% of base peak) 164 (0.6), 146 (96), 97 (80), 79 (100), 77 (97).

Registry No.—1, 56030-45-6; 2, 598-19-6; 3, 56030-46-7; 4, 56030-47-8; 5, 56030-48-9; *tert*-butyllithium, 594-19-4.

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(1) See E. J. Corey and R. L. Danheiser, *Tetrahedron Lett.*, 4477 (1973), and previous papers cited therein.
(2) E. J. Corey, D. E. Cane, and L. Libit, *J. Am. Chem. Soc.*, **93**, 7016 (1971).
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(4) M. Schlosser and E. Hammer, *Helv. Chim. Acta*, **57**, 2547 (1974).
(5) L. F. Hatch, H. E. Alexander, and S. D. Randolph, *J. Org. Chem.*, **15**, 654 (1950).
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(7) This work was assisted financially by a grant from the National Science Foundation.

Dehydrobromination of α-Bromo Ketones with Palladium Tetrakis(triphenylphosphine)

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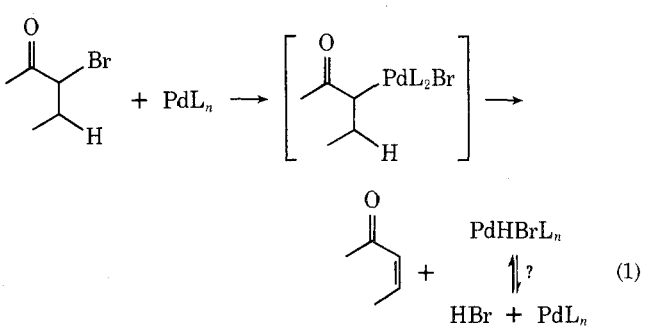
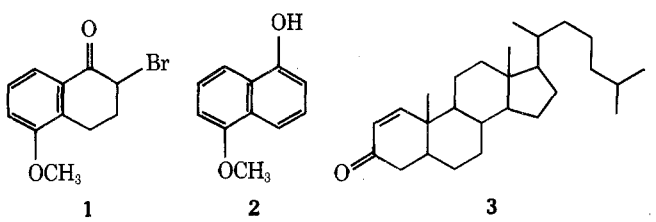
The conversion of ketones to α,β-unsaturated ketones is important in organic synthesis. The most widely used pathway for this transformation has consisted in preparation and dehydrohalogenation of intermediate α-bromo ketones. These dehydrobrominations usually require quite vigorous conditions.[1] This note reports our attempts to develop a mild method for this type of elimination using palladium tetrakis(triphenylphosphine).[2]

It was hoped that $Pd(PPh_3)_4$ would undergo facile oxidative addition with α-bromo ketones just as Pd(0) complexes do with other organic halides.[3] The resulting species, for which one possible representation is shown in eq 1,[4,5] might be expected to expel a β hydrogen along with palladium to form enone.[6] Presumably, the intermediate(s) involved would be similar to those in the direct oxidation of ketones to enones using Pd(II) salts.[7-9] The proposed method offers the potential advantage of regioselectivity in enone formation and could, in principle, be catalytic in palladium without added Cu(II) salts.[7,9]



(1)

The method works well in the case of 2-bromo-1-tetralones, where the initially formed enone can aromatize simply by tautomerization. When 5-methoxy-2-bromo-1-tetralone (1) is treated with 1 equiv of $Pd(PPh_3)_4$ in benzene under nitrogen, it is converted to 5-methoxy-1-naphthol (2)



1 2 3

Table I
Dehydrobromination of α-Bromo Ketones with $Pd(Ph_3P)_4$

α-Bromo ketone (registry no.)	Product(s) (% yield)	Conditions[a]
1	**2**[b] (94)	PhH, N_2, Et_3N (1.1 equiv),[c] 40°, 1.5 hr[c]
2-Bromo-1-tetralone (13672-07-6)	1-Naphthol[b] (90-15-3)	PhH, N_2, room temp, 3 min[d]
2α-Bromocholestan-3-one (23737-88-4)	**3** (~40) Cholest-4-en-3-one (~15) Cholestan-3-one (~35)	PhH, N_2, 80°, 2 hr
4α-Bromocholestan-3-one (56245-74-0)	Cholest-4-en-3-one (36) Mixture of **3** and cholestan-3-one (45)	PhH, N_2, 50°, 12 hr[e]
2-Bromocyclododecane (31236-94-9)	Mixture of *cis*- and *trans*-cyclododecenone (~50)	PhH, N_2, Et_3N (1.3 equiv),[c] room temp, 6 hr
2-Bromocyclohexanone (822-85-5)	Cyclohexenone (70)[f] Cyclohexanone (22)[f]	PhH, N_2, room temp, 8 hr

[a] 1 equiv $Pd(PPh_3)_4$ unless otherwise noted. [b] Only product by TLC. Registry number of 1-naphthol is in parentheses. [c] Reference 8. [d] Time of reaction varied considerably depending on the $Pd(PPh_3)_4$ used. [e] 2 equiv of $Pd(PPh_3)_4$. [f] GLC yield, not isolated.

quantitatively by TLC (94% isolated yield) with a reaction time varying from 3 min to 2 hr depending on the particular preparation of $Pd(PPh_3)_4$ used. 2-Bromo-1-tetralone is equally effectively dehydrobrominated to 1-naphthol. Appropriate control reactions were run to determine that the palladium reagent is indeed essential for the dehydrobrominations.

The method is less successful, however, with α-bromo ketones which cannot lead directly to phenolic products. Treatment of 2-bromocyclohexanone with $Pd(PPh_3)_4$ at room temperature for 8 hr gave 70% cyclohexenone and 22% cyclohexanone (GLC yields). Other examples are given in Table I. The steroidal cases, it should be noted, required more vigorous conditions and gave useless mixtures of products, with a disappointing lack of regiospecificity.

Numerous experiments were tried in an effort to make the nontetralone dehydrohalogenations efficient. For example, triethylamine was added to take up hydrogen bromide, which could act as a proton source to facilitate formation of saturated ketone, but this had no effect.[10] Similarly, addition of norbornadiene to take up hydrogen had no effect. Other Pd(0) and Pd(II) complexes, e.g., palladium bis(dibenzylideneacetone)[11] and palladium acetoacetonate,[12] were ineffective even for dehydrobromination of **1**. Pure cholest-1-en-3-one (**3**) was placed in a reaction of **1** with $Pd(PPh_3)_4$ to see if reversibility of hydrogen loss (which would be indicated by formation of cholestan-3-one) in systems which cannot go on to naphthol might be responsible for the low yield of enone in the steroidal cases, but the **3** was recovered unchanged. Use of less than 1 equiv of $Pd(PPh_3)_4$ in reaction with **1** resulted in lower yields of **2**; dehydrobromination catalytic in palladium was not observed.

Several interesting unanswered questions remain concerning the potential of this dehydrobromination method. In particular, one would like to know why the tetralones undergo elimination uniquely effectively among the substances used.[13] However, our motivation to pursue this research further was significantly reduced by the recent reports of the development of an efficient, mild, and apparently versatile preparation of α,β-unsaturated ketones from ketones via α-selenium derivatives.[14-16]

Experimental Section

Melting points were determined in open capillaries on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 137 or 333 spectrometer. The benzene used was distilled and stored over 4 Å molecular sieves, and had nitrogen bubbled through it before use.

Palladium Tetrakis(triphenylphosphine). The $Pd(PPh_3)_4$ was prepared either by Fitton's modification[17] of the procedure of Malatesta and Angoletta,[2] or, more conveniently, by the method of Takahashi,[18] which is described here. The recent preparation reported by Coulson[19] would presumably be the current method of choice. A mixture of 0.533 g (0.96 mmol) of palladium bis(dibenzylideneacetone)[11] and 2.133 g (8.1 mmol) of triphenylphosphine in 25 ml of benzene was stirred for 1 hr. The mixture was evaporated in vacuo and the residue was washed with 4 × 10 ml of anhydrous ether to afford 0.970 g (89%) of $Pd(PPh_3)_4$ as a bright yellow powder: mp 109–115° dec (lit.[18] mp 106° dec, lit.[20] mp 104–106° dec, lit.[19] mp 116° dec); ir essentially identical with that of PPh_3 from 4000 to 650 cm^{-1}, but has single band at 500 cm^{-1} vs. bands at 510 and 490 cm^{-1} for PPh_3. The $Pd(PPh_3)_4$ was usually used as prepared, since recrystallization[18] proved troublesome in our hands. Representative dehydrobromination experiments follow.

Conversion of 2-Bromo-5-methoxy-1-tetralone (1) to 5-Methoxy-1-naphthol (2). A mixture of 0.123 g (0.48 mmol) of **1**, mp 91–93°,[21] 0.558 g (0.50 mmol) of $Pd(PPh_3)_4$, and 0.53 g (0.53 mmol) of distilled triethylamine in 20 ml of benzene was stirred under nitrogen at 50° for 1.5 hr. The mixture was diluted with ether and extracted three times with 1 *M* NaOH solution. The extracts were acidified to pH 1 with 6 *M* HCl and extracted three times with ether. The ether layers were washed with brine, dried ($MgSO_4$), and evaporated to afford 0.078 g (94%) of **2**, which had an ir spectrum identical with that of an authentic sample.[22]

Conversion of 2-Bromocyclohexanone to Cyclohexenone. A mixture of 0.143 g (0.81 mmol) of 2-bromocyclohexanone[23] and 0.933 g (0.81 mmol) of $Pd(PPh_3)_4$ in 30 ml of benzene was stirred under nitrogen at room temperature for 8 hr. The mixture was filtered to remove 0.196 g of a yellow-orange precipitate, tentatively identified as $Pd(PPh_3)_2Br_2$ by the similarity of its ir spectrum to that of $Pd(PPh_3)_2Cl_2$[24] and by mp 270–275° dec (lit.[25] ca. 250° dec). The filtrate was reduced in volume to ca. 15 ml by distillation and 0.082 g of *o*-dichlorobenzene was added as an internal standard previously calibrated with known mixtures[26] for instrument response in GLC analysis. Using a Perkin-Elmer Model 154 vapor fractometer with a 20% SE-30 column at 130°, the GLC analysis indicated that the product contained 70% cyclohexenone and 22% cyclohexanone by comparison of retention times with those of authentic samples.[26]

Conversion of 4α-Bromocholestan-3-one to Cholest-4-en-3-one. A mixture of 0.120 g (0.26 mmol) of 4α-bromocholestan-3-one[27] and 0.601 g (0.52 mmol) of $Pd(PPh_3)_4$ in 25 ml of benzene was stirred under nitrogen at 50° for 12 hr. TLC indicated three principal products: cholestan-3-one, cholest-1-en-3-one, and cholest-4-en-3-one. The reaction mixture was filtered, and the filtrate was diluted with hot hexane and washed with 2 × 100 ml of hot water. The water was extracted with hot hexane and the combined organic layers (ca. 300 ml) were washed with brine, filtered, and evaporated to afford 0.522 g of yellow-brown solid, which ir indi-

cated was mostly triphenylphosphine oxide. A 0.190-g portion of this material was subjected to preparative TLC on silica gel, using 1:4 ether–hexane three times, to afford 0.012 g (36%) of cholest-4-en-3-one, mp 69–73° (lit.[28] mp 81–82°), identified by ir spectrum. From the preparative TLC there was also obtained 0.016 g of a mixture of cholestan-3-one and cholest-1-en-3-one.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—1, 31236-91-6; 2, 3588-80-5; palladium tetrakis(triphenylphosphine), 14421-01-3.

References and Notes

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(6) Elimination of H and a Pd species from π-allyl complexes of steroidal enones to form dienones has been reported: R. W. Howsam and F. J. McQuillin, *Tetrahedron Lett.*, 3667 (1968); I. T. Harrison, E. Kimura, E. Bohme, and J. H. Fried, *ibid.*, 1589 (1969).
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(10) Triethylamine is included in some of the reaction mixtures described in Table I and in the Experimental Section because it was erroneously believed for a short period that Et_3N had some beneficial effect on the dehydrobromination reaction.
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(13) The reactions of the nontetralone α-bromo ketones are reminiscent of the reactions of α-bromo esters with $Pt(PEt_3)_3$, which are reported to be mechanistically complex: A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7832 (1974), and references cited therein. Perhaps a cleaner, regiospecific dehydrohalogenation could be achieved by use of compounds and conditions which favor a straightforward S_N2 type of oxidative addition; see, e.g., P. K. Wong, K. S. Y. Lau, and J. K. Stille, *ibid.*, **96**, 5956 (1974).
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Complex Formation Between Potassium Acetate and a Simple Triol

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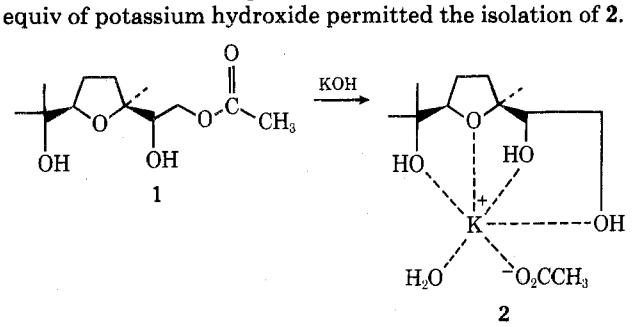
Complexes of organic compounds with metal ions have been known and studied for many years, but alkali metal ions have not been prominent in these studies until recently. The crown ethers[1] have been in the forefront of research on alkali metal ion complexes, and the first crown ethers have spawned a host of related compounds.[2,3] Other organic compounds[4–7] have shown a more limited capacity for complexing with alkali metal ions, and a number of naturally occurring polyether antibiotics[8–10] have shown remarkable selectivity for specific ions.

Most of the polyether molecules have a systematic configuration of ether, carbonyl, hydroxyl, and/or carboxyl groups that hold the ion in place, while the rest of the molecule serves to shield the ion, and give the overall complex more lipophilic character. X-Ray analysis of the structures of these complexes shows that often six ligand atoms are used in holding sodium and potassium ions. Six is not a magic number, but seems to be the frequent compromise between steric and electrostatic factors. An increasing number of ligands gives a more diffuse electrostatic interaction, but this is countered by the steric requirement of the ligands and their need to approach within a given distance of the ion.[11] The ligand atoms are frequently separated by two-carbon bridges. These consistent elements of structure[12] have made it possible to devise new compounds that show the capacity to complex, and this in part explains the proliferation of activity in this area.

We have observed a potassium acetate complex **2** involving a very small organic compound that has little more than the necessary elements of structure of the polyether ionophores. The four oxygen atoms in the triol have the characteristic two-carbon separations, with a water molecule and the acetate ion apparently functioning as additional ligands. The synthesis of **1** has been previously reported[13] using a neutral permanganate oxidation of geranyl acetate. These workers hydrolyzed **1** to the free triol using a fractional amount of potassium hydroxide. Our use of 1 equiv of potassium hydroxide permitted the isolation of **2**.



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