7. Distillation at 120 °C (0.03 mm) gave a 54.7% yield of a colorless liquid which solidified upon standing. The compound was further purified by sublimation at 90 °C (0.03 mm) to give **7a**, a white solid, mp 53–54 °C.

Reaction of 1-Dimer[3b] or 8 with Refluxing Anhydrous Methanol. Approximately 0.5 g of the appropriate dimer was placed in 50 ml of methanol, and the solution was heated to reflux for 30 min. Upon cooling, the respective dimer crystallized and was identified by comparing its melting point and NMR spectrum to those of the authentic compound. No other products were detected.

Reaction of 5 with Allyl Alcohol. To a clean, dry, 25-ml round-bottom flask flushed with dry nitrogen and capped with a rubber septum were added 2.11 g (0.0188 mol) of **5** and 5 ml of dry methylene chloride by means of a syringe. After the contents of the flask were stirred to ensure solution, 1.17 g (0.0200 mol) of anhydrous allyl alcohol was added in one portion by means of a syringe. The sample was stirred and allowed to stand at room temperature for 7 days, at which time an NMR spectrum of the solution showed no cyclopropenyl hydrogens present. The sample was diluted with 25 ml of ether, and 0.74 g (35.0% yield) of a white solid was recovered. This compound was identified as the dimer, **8**, by comparing its melting point, IR, and NMR spectra to that of the authentic compound. The ether–methylene chloride solution was concentrated to about 1 ml in volume by distillation at room temperature and reduced pressure. High vacuum distillation yielded 0.91 g (28% yield) of a colorless liquid which boiled at 38–42 °C (0.1 mm). This compound was identified as the allyl alcohol adduct, **10**, on the basis of IR, NMR, and mass spectral analysis. The NMR spectrum gave peaks at δ 1.15–2.28 (2 H, m), 3.28–4.05 (6 H, m), and 4.53–5.74 (6 H, m). The IR spectrum (neat) gave absorbances at 3108 (m), 3093 (m), 2971 (s), 2936 (s), 2892 (s), 1647 (m), 1468 (m), 1407 (s), 1367 (m), 1292 (m), 1238 (s), 1117 (s), 1063 (s), 1027 (s), 969 (m), 922 (m), and 856 cm^{-1} (w). The mass spectrum gave major ion fragments at *m/e* (rel abundance) 143 (1.2), 129 (1.2), 114 (3.8), 113 (42.2), 100 (1.9), 87 (2.5), 86 (5.0), 85 (6.3), 73 (6.9), 71 (2.3), 69 (2.3), 58 (12.0), 57 (39.0), 56 (10.7), 55 (100.0), 43 (5.0), 42 (6.3), 41 (40.8), 39 (15.7), 31 (18.9), 29 (13.8), 28 (25.2), and 27 (28.3). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.34; H, 8.26.

Reaction of 6 with Allyl Alcohol. This compound was treated with allyl alcohol by employing the same procedure as reported for **5** and allyl alcohol. No dimeric product was obtained upon the addition of ether. After the ether and methylene chloride were removed at reduced pressure and room temperature, several milliliters of a light straw colored oil remained. Distillation at 38 °C (0.04 mm) gave a 40% yield of a colorless liquid which was identified as the allyl alcohol adduct, **11**, by analysis of its spectra.

Acknowledgments. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, for which we are grateful. One of us (P.L.L.) also received financial support from the National Science Foundation Undergraduate Research Participation Program, summer 1973.

Registry No.—**1**, 60935-33-3; **2**, 60935-34-4; **3**, 60935-35-5; **3a**, 60935-36-6; **3b**, 42216-96-6; **4**, 60967-61-5; **4a**, 60935-37-7; **4b**, 60935-20-8; **5**, 60935-21-9; **6**, 60935-22-0; **6a**, 60935-23-1; **7**, 60935-24-2; **7a**, 60935-25-3; **8**, 60935-26-4; **9**, 60935-27-5; **10**, 60935-28-6; **11**, 60935-29-7; methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; 2-bromomethyl-2-chloromethyl-1,3-dioxane, 60935-30-0; 1-bromo-3-chloro-2,2-dimethoxypropane, 22089-54-9; 1,3-propanediol, 504-63-2; 2-bromomethyl-2-chloromethyl-5,5-dimethyl-1,3-dioxane, 60935-31-1; 2,4,8,10-tetraoxaspiro[5.5]-3,9-di(bromomethyl)-3,9-di(chloromethyl)undecane, 60935-32-2; pentaerythritol, 115-77-5; allyl alcohol, 107-18-6; 2,2-dimethyl-1,3-propanediol, 126-30-7.

Supplementary Material Available. Mass spectra of orthoacrylates and additional NMR and mass spectral data (8 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) To whom correspondence should be addressed.
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Direct Oxidation of Tertiary Allylic Alcohols. A Simple and Effective Method for Alkylative Carbonyl Transposition[1]

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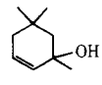
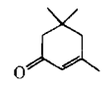
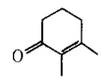
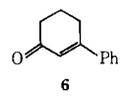
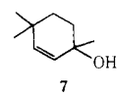
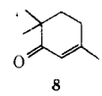
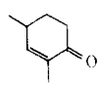
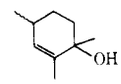
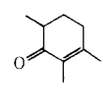
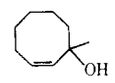
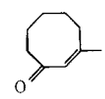
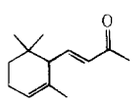
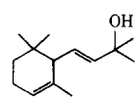
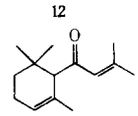
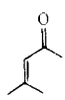
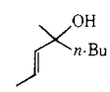
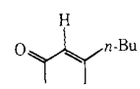
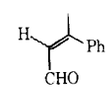
The oxidation of cyclic tertiary allylic alcohols, generated by the 1,2 addition of organometallic reagents to α,β-unsaturated cyclic ketones, with pyridinium chlorochromate (PCC) affords transposed 3-alkyl α,β-unsaturated ketones in excellent yield. Acyclic tertiary allylic alcohols also undergo this rearrangement in fair to good yields. Tertiary allylic alcohols generated by the addition of vinylmagnesium bromide to saturated ketones can be oxidized to the corresponding α,β-unsaturated aldehydes in good to excellent yield with PCC.

The ability to transpose a functional group efficiently from one carbon to another, as in 1,3-carbonyl transposition of α,β-unsaturated ketones, offers a wide degree of latitude in synthetic design of many naturally occurring compounds. In recent years a number of synthetic methods and reagents have become available for effecting this type of functional exchange. Among the methods commonly employed are included allylic interconversion of oxygen with selenoxide,[2] sulfoxide,[3] and amine oxides[4] via 2,3-sigmatropic rearrangements and the Wharton epoxy ketone rearrangement.[5] The formation and subsequent rearrangement of isoxazoles[6] has also been used to accomplish this exchange of functionality. In general, however, these methods suffer from inferior yields and/or multistep manipulation of delicate intermediates.

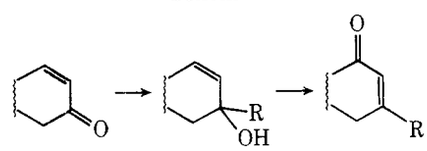
In a variation on this theme, Trost[7] has recently developed a procedure by which tertiary allylic alcohols, generated by the 1,2 addition of an organometallic reagent to an α,β-unsaturated ketone, are converted in several steps to new,

Table I. Intramolecular Alkylative-1,3-Carbonyl Transposition

Starting enone[k]	Alkyllithium Reagent	Allylic Alcohol[l]	Yield,[a] %	Transposed enone[m]	Yield[b]
	MeLi	 1	96	 2	94
	MeLi	 3	90	 4	93
	PhLi	 5	91	 6	90
	MeLi	 7	95	 8	98
	MeLi	 9	81	 10	84
	MeLi	 11	93	 12	88
	MeLi	 13	96	 14	31[c,d]
	*n*-BuLi	 15	90	 16	50[c,e]
	PhLi	 17	85	 18	51[c,f,g,h,i] 50[f,i,j]

[a] Crude yield. [b] Isolated yield, not optimized. [c] Yield determined by vapor phase chromatography. [d] 3 equiv of PCC and 16 h reaction time used. [e] ~4:3 mixture of *E* and *Z* isomers, respectively. [f] Yield based on recovered starting material. [g] A 35% yield of acetophenone also isolated. [h] ~4:1 mixture of *E* and *Z* isomers, respectively. [i] 3 equiv of PCC used. [j] Solid anhydrous sodium acetate added to buffer the reaction medium. [k] Registry no. are, respectively, 4694-17-1, 1121-18-2, 930-68-7, 1073-13-8, 40122-96-1, 1728-25-2, 127-41-3, 625-33-2, 78-94-4. [l] Registry no. are, respectively, 37779-25-2, 51036-24-9, 60174-90-5, 60934-84-1, 53846-74-5 (*cis*-**9**), 53846-76-7 (*trans*-**9**), 51783-32-5, 60934-85-2, 60934-86-3, 6051-52-1. [m] Registry no. are, respectively, 78-59-1, 1122-2-9, 10345-87-6, 23438-77-9, 20030-29-9, 60934-87-4, 31089-97-1, 60934-88-5, 21866-70-6 (*E*-**18**), 21878-52-4 (*Z*-**18**).

Scheme I

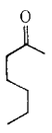
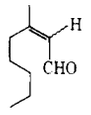
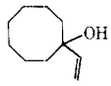
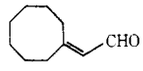
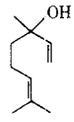
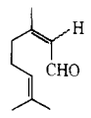


transposed β-alkyl conjugated ketones (Scheme I). This exchange of functionality has also been achieved by acid-catalyzed[8] rearrangement of the allylic alcohol followed by hydrolysis and oxidation. However, the direct oxidation of tertiary allylic alcohols has received only scant attention. In the steroids, various tertiary allylic alcohols upon oxidation yield either transposed α,β-unsaturated ketones and/or epoxy ketones depending on the stereochemistry of the initial hydroxy group.[9a-c] In simpler systems it has been demonstrated that Jones oxidation of substituted tertiary allylic alcohols affords the transposed unsaturated ketones in poor to moderate yield.[9d-h]

In recent years, a number of mild oxidizing reagents, compatible with a variety of acid-sensitive functional groups, have become available[10] and in this present investigation, the results of a study dealing with the scope and limitations of the oxidation of tertiary allylic alcohols with pyridinium chlorochromate[11] are reported. The overall result of the reaction sequence, as outlined in Scheme I, is an efficient method for alkylative carbonyl transposition which offers a number of advantages including mildness of reaction conditions and ease of operation.

It has been found that oxidation of cyclic allylic tertiary alcohols with 2 equiv of pyridinium chlorochromate in dichloromethane affords the transposed α,β-unsaturated ketones in good to excellent isolated yields (see Table I). For example, oxidation of 1-methylcyclooct-2-en-1-ol gave 3-methylcyclooct-2-en-1-one in 88% yield, uncontaminated with its more stable β,γ isomer. Use of the Jones reagent[12] as the oxidant, with this compound, gave a mixture of α,β- and β,γ-enones (4:3, respectively) in 48% yield. Acyclic allylic

Table II. Intermolecular Alkylative 1,3-Carbonyl Transposition

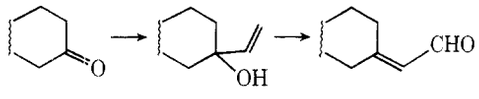
Ketone[g]	Allylic alcohol[h]	Yield,[a] %	α,β-Unsaturated aldehyde[i]	Yield,[b] %	Recovered starting material, %	Other products (%)
	 19	86	 20	90[a,c]	20	2-Heptanone (7)
	 21	71	 22	89[a]	25	Cyclopentanone (5)
	 23	86	 24	83[d]	29	Cyclohexanone (7)
	 25	85	 26	73[d]	24	Cyclooctanone (15)
				54[d,f]	0	Cyclooctanone (20)
	 27		 28	86[c,d,e]	50	6-Methylhept-5-en-2-one (3)
				78[a,c,f]	≤2	6-Methylhept-5-en-2-one (2)

[a] Isolated yield. [b] Based on recovered starting material. [c] ~2:1 mixture of *E* and *Z* isomers, respectively. [d] Yield determined by vapor phase chromatography. [e] Solid anhydrous sodium acetate added to buffer the reaction medium. [f] 3.5 equiv of PCC and 48 h reaction time used. [g] Registry no. are, respectively, 110-43-0, 120-92-3,108-94-1, 502-49-8. [h] Registry no. are, respectively, 24089-00-7, 3859-35-6, 1940-19-8, 6244-48-0, 78-70-6. [i] Registry no. are, respectively, 60934-89-6 (*E*-**20**), 60934-90-9 (*Z*-**20**), 5623-82-5, 1713-63-9, 7071-24-1, 5392-40-5.

tertiary alcohols also afforded transposed α,β-unsaturated ketones, albeit in lower yield and contaminated with unusual side products. For example, oxidation of 2-phenylbut-3-en-2-ol afforded a 35% yield of acetophenone in addition to the transposed aldehyde. Two allylic alcohols examined, 2-(1′-cyclohexenyl)propan-2-ol and 4-(2′,6′,6′-trimethylcyclohex-1-enyl)-2-methylbut-3-en-2-ol, failed to give useful yields of transposed products.

An obvious extention of this reaction sequence, the oxidation of tertiary allylic alcohols generated by the condensation of saturated ketones with vinylmagnesium bromide,[13] has also been examined. The net effect of the process, as outlined in Scheme II, is a simple and effective method for the formation

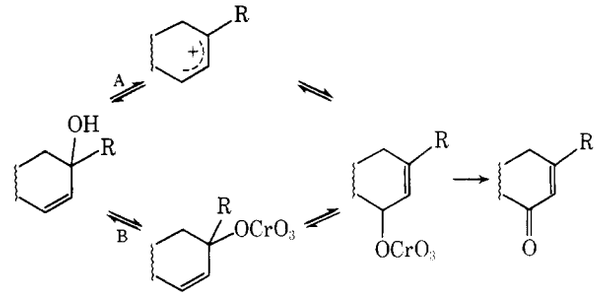
Scheme II



of α,β-unsaturated aldehydes.[14] The results of this study are reported in Table II and reveal that α,β-unsaturated aldehydes were obtained in good yield, based upon recovered starting material. Extended reaction times and increased oxidant levels had unpredictable effects. Thus, oxidation of linalool with 3.5 equiv of pyridinium chlorochromate (in place of the standard 2 equiv) for 48 h led to a 78% isolated yield of citral (>96% pure), whereas oxidation of 1-vinylcyclooctan-1-ol under similar conditions gave the α,β-unsaturated aldehyde in lower yield than found under less forcing conditions.

While it is premature to speculate on the detailed mechanism of this oxidation, conceptually at least, there are two pathways which may be operating (Scheme III). Owing to the acidic nature of pyridinium chlorochromate,[15] it is possible that there may be a prior solvolysis of the tertiary alcohol to an allylic carbonium ion which subsequently collapses with a chromate ion at the lesser substituted termini to generate

Scheme III



an isomeric chromate ester which undergoes oxidation, as in path A. Alternatively, tertiary chromate ester formation may precede rearrangement (either stepwise or concerted), as in path B. Presently, this latter pathway appears to be in operation for the following reasons: (1) the use of buffered conditions had no effect on the oxidation; (2) attempted oxidation of 2-cyclopropylpropan-2-ol, a system known to undergo carbonium ion rearrangements,[16] afforded, at most, trace amounts (≤2%) of the transposed aldehyde, the major product being 5-chloro-2-methylpent-2-ene (~40%) in addition to recovered starting material, even after extended periods of reaction; (3) finally, the transposition–oxidation reaction was effected equally well using the basic Collins[17] reagent. In fact, using 1,4,4-trimethylcyclohex-2-en-1-ol as a standard substrate, the relative effectiveness of the Jones,[9] Collins,[17] and Corey[11] oxidizing reagents were examined and it was found that the yields of the transposed α,β-unsaturated ketones were 76, 94, and 97%, respectively.

Thus, the readily available pyridinium chlorochromate[18] can effect oxidation of tertiary allylic alcohols to the corresponding transposed α,β-unsaturated carbonyl compounds in good to excellent yields, making the overall reaction process a useful synthetic method for alkylative 1,3-carbonyl transposition.

Experimental Section

Unless otherwise noted, the following general conditions were used in all reactions. Infrared spectra were recorded using either a Perkin-Elmer 137 Infracord or 710 grating spectrometer. NMR spectra were obtained with a Varian T-60 or Perkin-Elmer R24B spectrometer with tetramethylsilane as an internal standard. Ultraviolet spectra were obtained on a Perkin-Elmer 202 spectrometer. Mass spectral analysis and exact mass determinations were obtained from the Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif. Unless otherwise noted, all reactions run in nonaqueous media were maintained under an atmosphere of purified nitrogen. Diethyl ether and tetrahydrofuran were purified by distillation from sodium benzophenone. Mallinckrodt reagent grade dichloromethane was used without further purification. The formation of isophorone is representative of the procedure followed.

1,5,5-Trimethylcyclohex-2-en-1-ol (1).[5] To a stirred solution of 5,5-dimethylcyclohex-2-en-1-one[19] (2.0 g, 16.1 mmol) in 20 ml of anhydrous ether at −78 °C was added, dropwise, an ethereal solution of methyllithium (11 ml of a 1.56 M ethereal solution). The resulting solution was allowed to warm to room temperature, stirred for 2.0 h, and quenched by the dropwise addition of 10 ml of water. The phases were separated and the aqueous layer extracted with two 10-ml portions of ether. The combined organic layers were washed with two 20-ml portions of water and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure to afford 2.15 g (96%) of a clear, colorless oil, judged by VPC[20] to be 97% pure. The alcohol was not purified further but used directly in the next step.

Isophorone (2). To a magnetically stirred slurry of pyridinium chlorochromate (4.30 g, 20.0 mmol) in 30 ml of dichloromethane, there was added in one portion a solution of 1 (1.40 g, 10.0 mmol) in 10 ml of dichloromethane at room temperature. The resulting dark red-black mixture was allowed to stir for 2.0 h at room temperature, and was diluted with an equal volume of ether. The ethereal solution was decanted from the black resinous polymer, which in turn was washed with three 20-ml portions of ether. The combined ethereal phases were washed successively with two 100-ml portions of 5% aqueous NaOH, 100 ml of 5% aqueous HCl, and two 50-ml portions of saturated aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure and the residue bulb to bulb distilled to afford 1.33 g (96%) of isophorone (≥97% pure), spectrally identical with an authentic sample.

Registry No.—**29,** 930-39-2; cyclopropyl methyl ketone, 765-43-5.

Supplementary Material Available. Detailed experimental and spectroscopic data (IR, NMR, UV, mass spectrum) for compounds **3, 7, 9, 13, 14, 15,** and **20** (11 pages). Ordering information is given on any current masthead page.

References and Notes

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(12) The procedure reported in ref 9d was followed. Use of acetone as the solvent affords a slightly higher yield, as a mixture of α,β- and β,γ-enones in a 3:7 ratio, respectively. M. Haenel, unpublished results.
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Structure Effects in the Oxidation of Alkenes by Solutions of Thallic Salts[1]

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The determination of polar, steric, and resonance effects in the oxidation of alkenes by solutions of thallic salts was carried out using the linear free energy relationship for the chosen set of $RCH{=}CH_2$, $R_1R_2C{=}CH_2$, and the internal alkenes; it was found that polar effects were the most important for the oxidation of $RCH{=}CH_2$ and $R_1R_2C{=}CH_2$ alkenes in this case. Both steric and resonance effects are important in the oxidation of internal alkenes. An aqueous medium is advantageous for the preparation of the carbonyl compounds from alkenes with electron-releasing substituents. The structure effects on the selectivity of the oxidation are discussed.

The oxidation of alkenes by thallic salts has been intensively studied from the point of view of the preparative organic chemistry,[2-7] as well as from theoretical aspects.[8-16] A more complete quantitative comparison of the influence of the individual parameters on the course of oxidation has been lacking so far.

The present investigation has been carried out to provide further information on the mechanism and the effect of structure on the rates of oxidation of alkenes by thallic salts, and on the distribution of products of the oxidation.

The kinetic behavior of the lower alkenes (C_2 to C_4) during their reaction with thallic salts along with the distribution of the oxidation products are described in the fundamental studies of Henry.[8] In aqueous medium, two characteristic products are formed by the oxidation of alkenes, viz. a carbonyl compound (an aldehyde or ketone) and vicinal diol. The