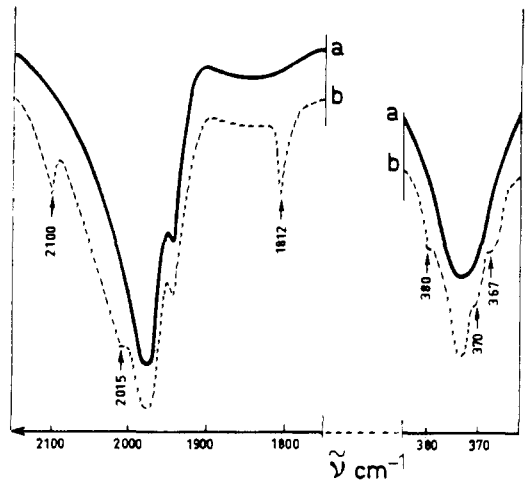


Figure 1. Infrared spectra, recorded on a Perkin 225 spectrometer of $W(CO)_6$ in CCl_4: (a) — before and (b) . . . after uv irradiation.

(i) The band at 373 cm^{-1} loses its symmetry and acquires shoulders at 367, 370, and 380 cm^{-1}. This result must indicate that the symmetry of the tungsten complex is diminished and suggests the formation of W-Cl bands, whose stretching vibration lies also at 373 cm^{-1}.[9]

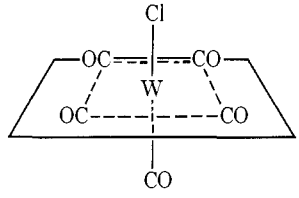
(ii) A new band appears at 1812 cm^{-1}. This band can be attribued to the carbonyl vibration in phosgene.[10]

(iii) Two new bands appear at 2100 and 2015 cm^{-1}. This observation seems to be in better agreement with the formation of $W(CO)_5Cl$ than with $W(CO)_4Cl_2$ which has been shown to have vibration frequencies at 2105, 2025, 1976, and 1935 cm^{-1}.[11] $W(CO)_5Cl$, however, belongs to a C_{4v} symmetry group and would be expected to have three CO stretching frequencies. It seems possible that the third, missing, absorption is masked by the strong vibrational band of $W(CO)_6$ at 1982 cm^{-1}. For comparison, two carbonyl bands at 2070 and 2016 cm^{-1} are found in the spectrum of $Mn(CO)_5Cl$.[12]

We propose then that the first step of this photochemical reaction involves the formation of $W(CO)_5Cl$, *via* a reaction between $W(CO)_5$ and the solvent, reaction between CO and the solvent would give phosgene.

The formation of $COCl_2$ is not equilibrated as is shown by the fact that the metathesis conversion ratio is not affected by the addition of $COCl_2$ in the reaction medium.

$$W(CO)_6 \xrightarrow{h\nu} W(CO)_5 + CO \xrightarrow{CCl_4} W(CO)_5Cl + COCl_2$$



In view of its low field effect the halogen atom will strengthen the trans CO group and labilize the cis CO groups, as has been observed in the case of the cis disubstitution of group VII halogeno carbonyl complexes by pyridine and aliphatic amines.[13] Hence in the subsequent steps of the reaction with $W(CO)_5Cl$, the two incoming olefin molecules will enter cis as is required for metathesis to proceed. Work on the characterization of the subsequent olefin-metal complexes is in hand.

This new type of olefin metathesis reaction is not only highly efficient but is also much "cleaner" than systems involving a cocatalyst, and should therefore constitute a useful model for the study of the key reaction intermediate and the factors which govern its formation and stability.[14]

Acknowledgment. We thank Dr J. S. Lomas for his help in the preparation of this manuscript and M. Billhot for technical assistance.

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(14) Experiments were carried out under dry argon atmosphere. Reactants (about 10^{-1} to 10^{-2} *M*) were irradiated by means an OSRAM Hg 10 lamp in a small thermostated quartz cell for 2–4 hrs. Products were analyzed by glpc on DC 200 column.

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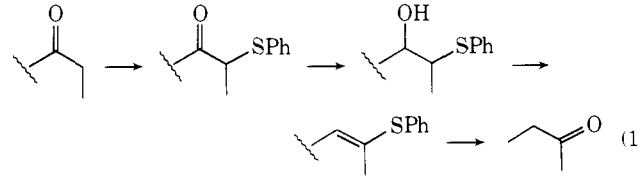
Received August 30, 1974

New Synthetic Methods. 1,2-(Alkylative) Carbonyl Transpositions

Sir:

The importance of the carbonyl group in organic synthesis makes the ability to relocate it within a molecule an important and challenging problem.[1] While previous work attacked the problem with respect to ketones, methods to transpose the carbonyl group of esters are lacking. The direct sulfenylation of esters and ketones with disulfides stimulated the utilization of such intermediates for this function.[2,3] Equation 1 illustrates the sequence.

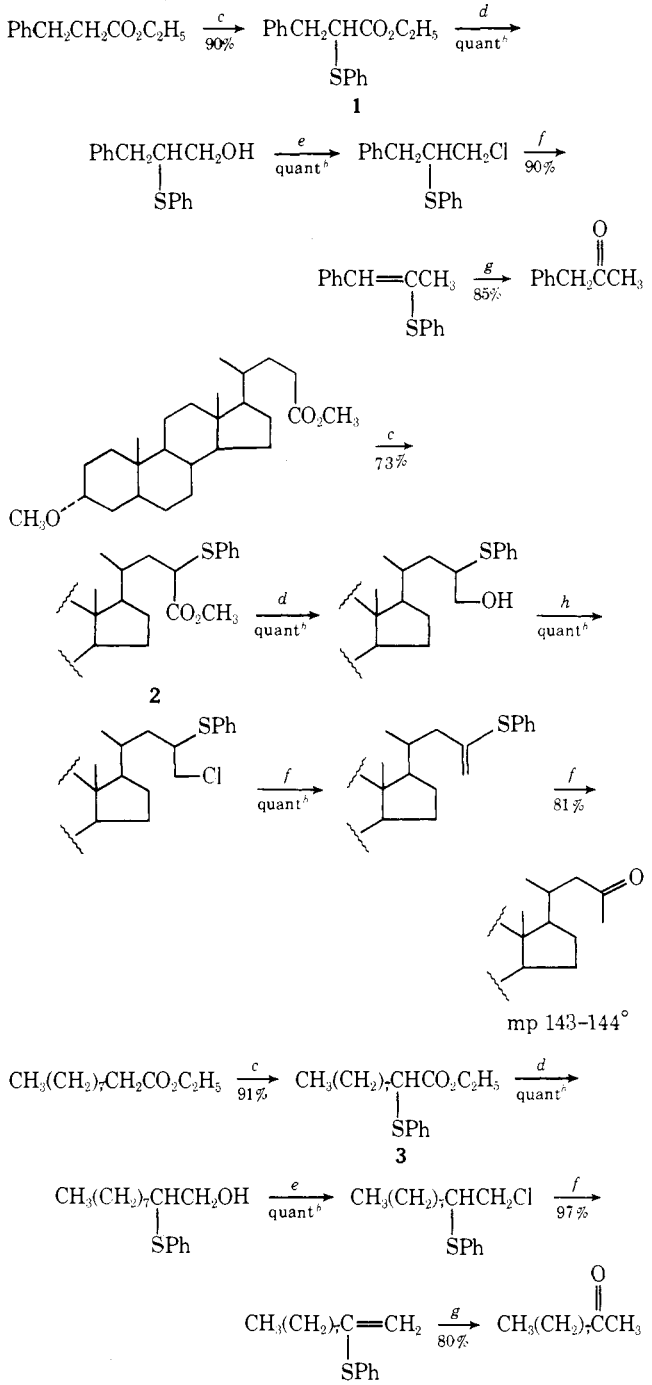


(1)

The α-sulfenylated esters **1**, **2**, and **3**, available as previously described[2a] (see Scheme I), were smoothly reduced to their alcohols with lithium aluminum hydride (THF, room temperature). Treatment with thionyl chloride at room temperature (benzene or ether) produced the primary chlorides which were dehydrohalogenated with potassium *tert*-butoxide in DMSO at room temperature. In the case of **1**, the initially produced olefin isomerized under the conditions to the thermodynamically more stable conjugated isomer.[4] Hydrolysis of the resulting enol thioethers was normally accomplished with mercuric chloride in 3:1 acetonitrile:water at reflux.[5] The overall yield for the process ranges from 60 to 75%.

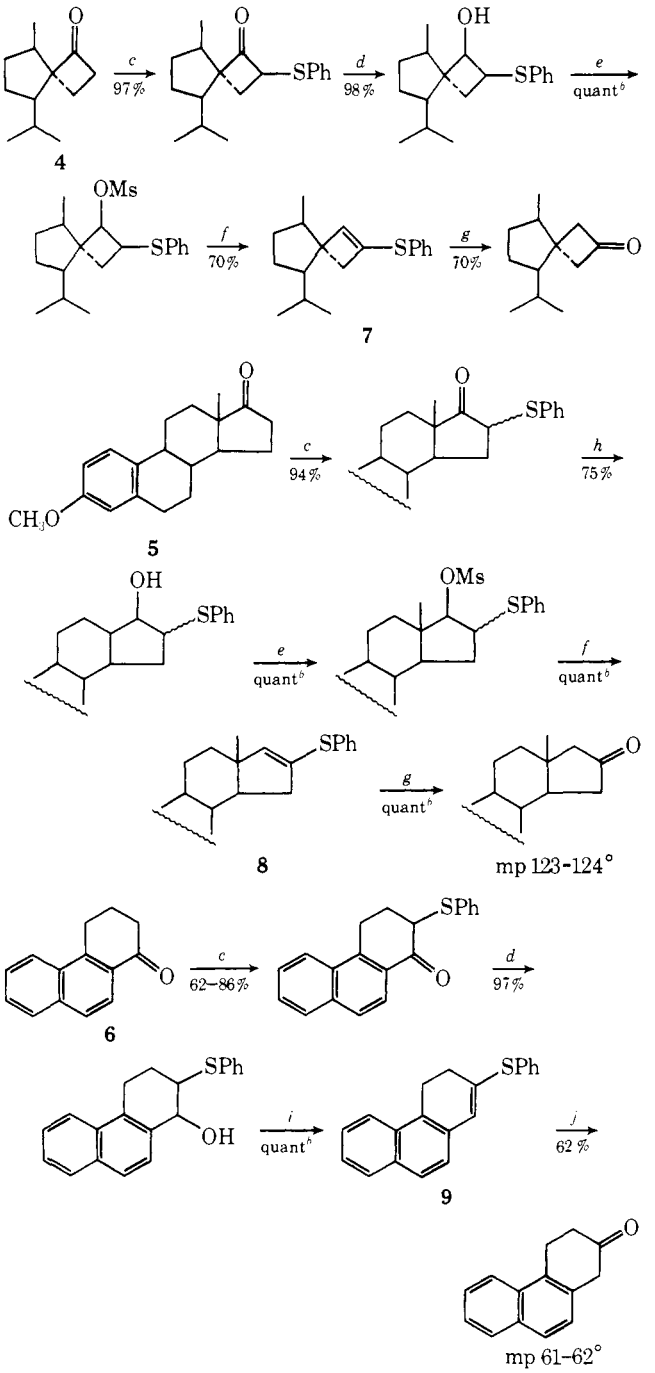
Application of a similar sequence to ketones **4**, **5**, and **6** also leads to net 1,2-carbonyl transposition. In these cases, reduction was accomplished with sodium borohydride in ethanol or methanol at room temperature. The dehydration sequence involved either refluxing a benzene solution of the alcohol in the presence of a catalytic amount of *p*-toluene-

Scheme I. Carbonyl Transposition of Esters[a]



[a] All new compounds have satisfactory spectral properties. [b] A quantitative yield. [c] Lithium *N*-cyclohexyl-*N*-isopropylamide, THF, −78°; PhSSPh, −25° and room temperature. [d] LAH, THF, room temperature. [e] $SOCl_2$, PhH, room temperature. [f] KOC_4H_9-*t*, DMSO, room temperature. [g] $HgCl_2$, $3CH_3CN$:$1H_2O$, reflux. [h] $SOCl_2$, ether, room temperature. [i] $HgCl_2$, 4 dioxane:$1H_2O$, reflux.

Scheme II. Carbonyl Transposition of Ketones[a]

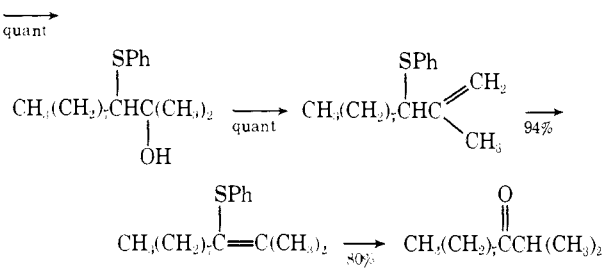


[a] All new compounds have satisfactory spectral properties. [b] A quantitative yield. [c] Lithium *N*-cyclohexyl-*N*-isopropylamide, THF, −78°; PhSSPh, HMPA, 0°. [d] $NaBH_4$, CH_3OH, room temperature. [e] CH_3SO_2Cl, pyridine, room temperature. [f] KOC_4H_9-*t*, DMSO, room temperature. [g] $HgCl_2$, $3CH_3CN$:$1H_2O$, reflux. [h] $NaBH_4$, C_2H_5OH, room temperature. [i] TsOH, PhH, reflux. [j] $TiCl_4$, HOAc, H_2O, reflux.

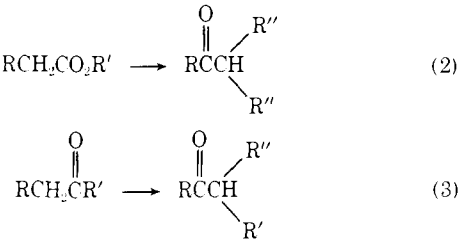
sulfonic acid with azeotropic removal of water or conversion to the mesylate (methanesulfonyl chloride in pyridine or triethylamine-methylene chloride at room temperature)[6] followed by base (potassium *tert*-butoxide, DMSO, room temperature). The former method is satisfactory for benzylic, allylic, or tertiary alcohols, whereas, the latter method is applicable to the cases of secondary alcohols. Hydrolysis of the enol thioethers proved to be the most troublesome step. In the cases of **7** and **8**, mercuric chloride in hot aqueous acetonitrile was effective. Hydrolysis of **9** required titanium tetrachloride in hot moist acetic acid.[7] The examples in Scheme II illustrate the applicability of the approach to four-,[8] five-, and six-membered rings in overall yields of 47-70%.

The versatility of the method is illustrated by the replacement of the hydride reduction with an organometallic addition to effect a net regiospecific alkylative carbonyl transposition. For example, sulfenylated ester **3** undergoes quantitative addition of methyllithium at room temperature in THF. While dehydration (TsOH, PhH, reflux) produces the β,γ olefin, exposure of this olefin to potassium *tert*-butoxide in DMSO at room temperature isomerizes it to the

enol thioether.[9] Hydrolysis under the standard conditions ($HgCl_2$, CH_3CN, H_2O, reflux) completes the sequence.



Equations 2 and 3 summarize the transformations achievable by these methods. In addition to effecting a 1,2



shift of the carbonyl group, the method allows for formation of additional carbon-carbon bonds at the former carbonyl group. A novel approach to unsymmetrical ketones from symmetrical ketones is embodied in the approach. Further applications of these methods are in progress.

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs. We thank the Syntex Corporation for a generous gift of estrone methyl ether.

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A Photolabile Protecting Group for Histidine

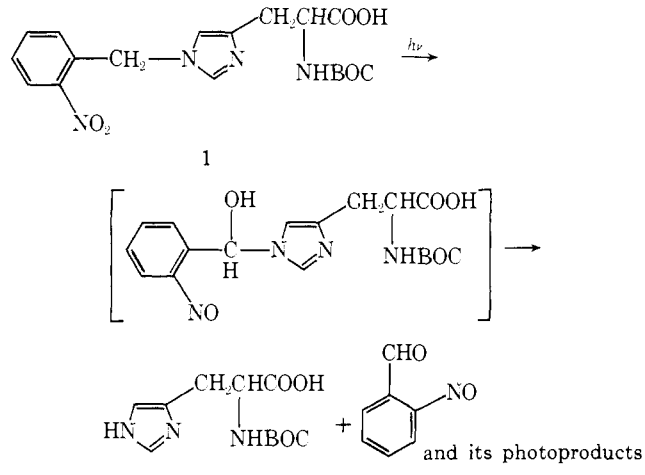
Sir:

We describe a method of introducing the *o*-nitrobenzyl group (ONB) into the imidazole side chain of histidine and its subsequent removal under mild, highly specific conditions by irradiation. This group has been used to block amino and carboxyl groups[1] and is stable under most of the conditions of peptide synthesis. Thus it is unreactive to anhydrous trifluoroacetic acid, anhydrous hydrogen chloride in acetic acid, and sodium hydroxide in methanol but is slowly cleaved by catalytic hydrogenation.

Although *im*-benzyl-L-histidine can be prepared by the reaction of benzyl chloride with the anion of the imidazole side chain, generated by sodium in liquid ammonia,[2] the reaction failed with *o*-nitrobenzyl chloride, resulting instead in the quantitative formation of 2,2′-dinitro-*trans*-stilbene.[3]

The *o*-nitrobenzyl group was introduced instead by reaction of the silver salt of N^{α}-*tert*-butoxycarbonyl-L-histidine methyl ester[4] with *o*-nitrobenzyl bromide in refluxing benzene for 4 hr. After removal of the silver bromide, the crude product was saponified by treatment with 2 equiv of 1 *N* NaOH in MeOH–DMF (3:1) for 2 hr. The solution was diluted with water, adjusted to pH 3.9 with HCl, saturated with NaCl, and extracted with ethyl acetate. N^{α}-Boc-N^{im}-ONB-L-His-OH was crystallized from ethyl acetate–petroleum ether in over-all yields of 60–70% for the three reactions and melted at 90° dec.[5] When the reaction was carried out with *o*-nitrobenzyl chloride in refluxing *p*-xylene, the starting material disappeared in 22 hr (tlc) but the over-all yield of the product was only 40–50%. The same compound was prepared by reaction of N^{α}-Boc-L-His-OMe with *o*-nitrobenzyl halides and dicyclohexylamine in DMF, followed by saponification, in yields of 30 and 45% for the chloride and bromide, respectively.[6]

To remove the *o*-nitrobenzyl group, a solution of **1** (3×10^{-3} *M* in dioxane) was irradiated with a mercury vapor



and its photoproducts