pear with very little if any additional splitting. The endo isomer of **3**, on the other hand, has dihedral angles for H-5, -6 and for H-7, -1 approximating 40°. Consequently considerable bridgehead-proton coupling is predicted with a correspondingly complex H-6, -7 pattern. Actually the nuclear magnetic resonance spectrum of the isopropylidene derivative **3** presents the signals for H-6 and -7 as an almost unperturbed, two-proton AB quartet. Accordingly the exo assignment is indicated.

Bicyclo compound **3**, treated with ozone under conditions such that the acid chloride grouping developed by ozonolysis reacts directly with methanol, forms the corresponding aldehyde ester. Without isolation, this is reduced with sodium borohydride to generate the methyl ester of (2,3-*O*-isopropylidene-β-ribofuranosyl)acetic acid (**4**) in 72% yield from **3**. A detailed nuclear magnetic resonance examination of this compound at 300 MHz gives results wholly consistent with formulation **4**. The ester is readily hydrolyzed (over 90%) to (2,3-*O*-isopropylidene-β-ribofuranosyl)acetic acid or to β-ribosylacetic acid itself. Acetic anhydride in hot pyridine cyclizes the isopropylidene acetic acid derivative to lactone **5** (77%),[7] and this with aminoguanidine bicarbonate[8] gives the 3-amino-1,2,4-triazole **6** (80%). Removing the protective group furnishes the free nucleoside **7** as the hydrochloride and thereby completes the synthesis. So far as we could determine this represents a new kind of nucleoside, for which we suggest the name, homo-C-nucleoside by extension from the name for the homonucleosides, *e.g.*, homouridine.[9]

The enolate of lactone **5** has proved to be a rich source of potentially useful intermediates. Utilizing this lactone enolate, we have succeeded in substituting the following groups on the position α to the lactone carbonyl: bromo, phenylmercapto, hydroxymethylene, carbomethoxy, and *N*-carbethoxythiocarbamyl. We anticipate that this general approach will provide a flexible general synthesis of C-nucleosides, homo-C-nucleosides, and related biologically important compounds. Work with the above mentioned derivatives as well as with others will be continued.

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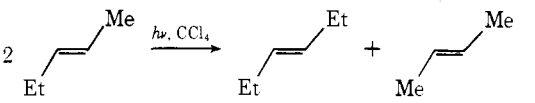
Photochemically Induced Olefin Metathesis by Transition Metal Complex. I. The Intermediacy of $W(CO)_5Cl$

Sir:

Although different structures have been proposed for the key intermediate in olefin metathesis,[1,2] it is generally agreed that the disubstituted complex must have two olefin molecules in a cis relationship. As demonstrated by Strohmeier[3] and recently by Wrighton,[4] the photochemically induced substitution of group VI hexacarbonyl, $M(CO)_6$, involves a first step leading to a short-lived intermediate, $M(CO)_5$, which reacts rapidly with an n or π donor, D, to give mono- and disubstituted compounds $M(CO)_5$ D and $M(CO)_4$ D_2, but it has been shown in the case of olefin π donors in *n*-hexane that the disubstituted compound has trans geometry.[5] Metathesis cannot therefore take place.

We wish now to report that olefin metathesis can be induced by uv irradiation of a transition metal complex in the presence of a suitable solvent, carbon tetrachloride.

Thus when a solution of *trans*-2-pentene and tungsten hexacarbonyl (20 mol per mole, excess olefin) is irradiated in CCl_4 at 25–50°, 2-butene and 3-hexene are obtained mainly in the trans form (*trans*-2-Butene:*cis*-2-Butene, 4:2) with a conversion ratio of about 50%, regardless of the temperature. The conversion ratio depends, however, slightly upon the olefin : $W(CO)_6$ ratio, falling from 59 to 50% as the molar ratio is raised from 1:1 to 20:1 (excess olefin). When CCl_4 is replaced by *n*-hexane no olefin metathesis is observed.



The most efficient wavelength for this reaction is at about 335 nm, which corresponds to an $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in the tungsten hexacarbonyl.[6]

Addition of *trans*-2-pentene in the dark to a previously irradiated $W(CO)_6$–CCl_4 solution leads also to metathesis; the metathesis reaction itself is therefore not purely photochemical. The aim of this work was to investigate the first photochemical step of the reaction.

Irradiation of $W(CO)_6$ in CCl_4 or in *n*-hexane, in the absence of olefins, gives rise to a yellow coloration, which is characteristic of the formation of the unstable $W(CO)_5$ species, whose absorption maximum lies at 410 nm.[7] This highly reactive species may then undergo reaction with the solvent.

The ir spectrum of the photoreaction product in *n*-hexane shows a symmetrical band at 373 cm^{-1} (W-C vibration), a strong band at 1982 cm^{-1} (CO vibration), and a shoulder at 1950 cm^{-1} (^{13}CO).[8] In the absence of any donor the $W(CO)_5$ reacts with CO and reverts to $W(CO)_6$.[7]

The ir spectra of $W(CO)_6$ in CCl_4 before and after uv irradiation reveal three main modifications as shown in Figure 1.

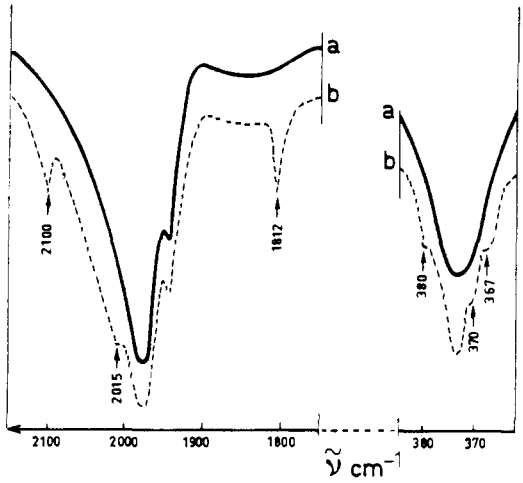


Figure 1. Infrared spectra, recorded on a Perkin 225 spectrometer of $W(CO)_6$ in CCl_4: (a) — before and (b) . . . after uv irradiation.

(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]

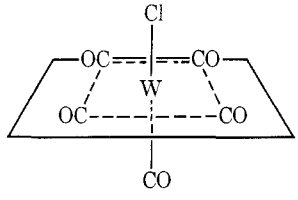
(ii) A new band appears at 1812 cm^{-1}. This band can be attribued to the carbonyl vibration in phosgene.[10]

(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]

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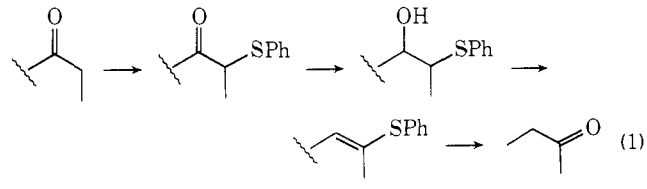
New Synthetic Methods. 1,2-(Alkylative) Carbonyl Transpositions

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.



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-