phosphoranes.[1,16] Nevertheless it is worth noting that at this point characteristic nmr parameters have not been established for the square pyramidal phosphorane geometry.[17]

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(9) More accurate measurement of the chemical shifts and coupling constants was precluded by the fact that the resonances overlap.

(10) Note that no $^{31}P{-}N{-}^{13}C$ coupling is observed. The two-bond $^{31}P{-}C{-}^{13}C$ coupling constant is very small (<0.1 Hz) in $CH_2 = CHP(O)Cl_2$ (W. Althoff and R. Schmutzler, private communication). These very small or zero coupling constants are due presumably to the facility with which two-bond phosphorus couplings undergo sign changes; see, *e.g.*, S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966); A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966); G. Mavel, *Progr. Nucl. Magn. Resonance Spectrosc.*, **1**, 251 (1966); W. McFarlane, *Chem. Commun.*, 58 (1967); D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, 819 (1967); E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 165 (1968); C. J. Jameson, *J. Amer. Chem. Soc.*, **91**, 6232 (1969); J. R. Schweiger, A. H. Cowley, E. A. Cohen, P. A. Kroon, and S. L. Manatt, *J. Amer. Chem. Soc.*, **96**, 7122 (1974).

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Synthesis of a Triazole Homo-C-nucleoside

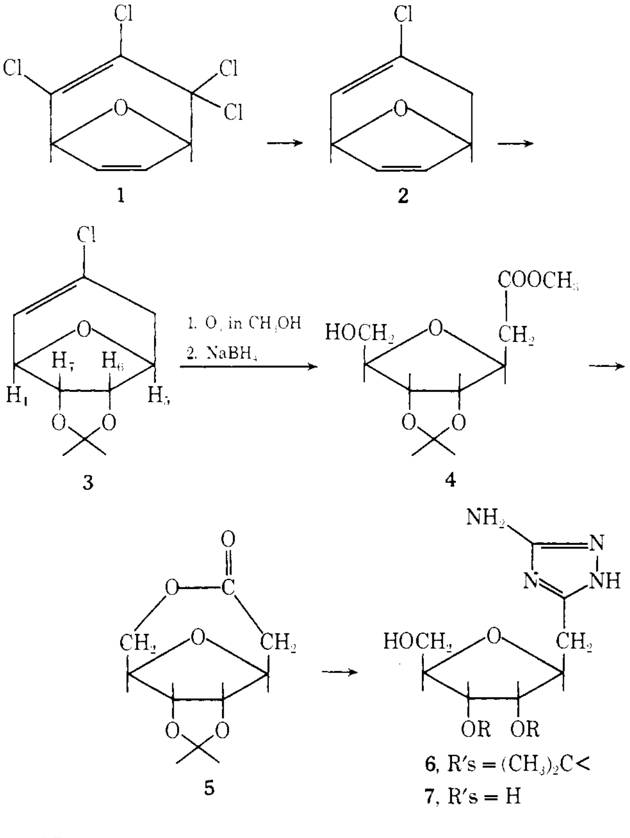
Sir:

With pseudouridine[1] as its first member, the group of compounds known as C-nucleosides has steadily increased.[2] Each of the compounds has biological properties of considerable importance and interest. Although a variety of syntheses are reported, practically all have been partial, involving D-ribose or some other sugar in some way.[3] We now wish to describe a stereospecific total synthesis approach, independent of natural ribose, which has furnished a new homo-C-nucleoside, and which promises to open a way to other related compounds.

The starting point is the readily accessible tetrachlorobicyclo compound **1**,[4] which on reduction with lithium aluminum hydride in the presence of lithium hydride loses three of its four chloro groups to give 3-chloro-8-oxabicyclo-[3.2.1]octa-2,6-diene (**2**)[5] in 80% yield. The expectation that the double bond in **2** that carries the chloro group ($\Delta^{2(3)}$) would be less readily attacked by electrophilic reagents than the unsubstituted double bond ($\Delta^{6(7)}$) was realized when diolefin **2** was found to react smoothly and selectively with osmium tetroxide–hydrogen peroxide and acetone to give the desired glycol (in the form of its isopropylidene derivative **3**) as the only product in 70% yield (Scheme I).

We have formulated adduct **3** with the oxygen substituents cis exo rather than cis endo for two reasons. First, examination of a Dreiding scale model of substrate **2** reveals that the exo side of the double bond offers more room for approach of the bulky reagent than the endo side. Second, a model of exo compound **3** has a dihedral angle between H-6 and the bridgehead H-5 measuring close to 90°. The same is true of the dihedral angle between H-7 and the bridgehead H-1. Accordingly, there should be minimal nuclear magnetic resonance coupling between H-5 and -6 as well as between H-1 and -7,[6] so that the quartet expected from the spin–spin coupled cis protons at positions 6 and 7 should ap-

Scheme I



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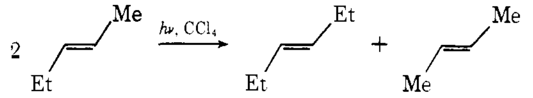
Photochemically Induced Olefin Metathesis by Transition Metal Complex. I. The Intermediacy of $W(CO)_5Cl$

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.