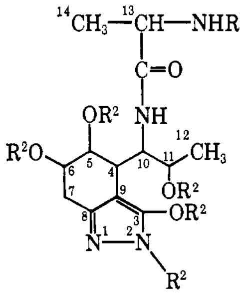

10, $R^1 = CH_3CO$; $R^2 = H$
11, $R^1 = R^2 = CH_3CO$

The immediate disappearance of two one-proton doublets (J = 4 cps) at δ 4.77 and 5.05 (in addition to the singlet for the enolic H at δ 13.15) in the nmr spectrum (DMSO-d_6) of **2** upon addition of deuterium oxide confirms the presence of two secondary hydroxyl groups. The formation of the tri-O-acetate **4** ($C_{21}H_{28}N_2O_{10}$; mp 175.0–175.5°; $[\alpha]^{25}D$ +29.4° (c 3.8, MeOH)) lends additional support, while the consumption of 1 mole of periodate by the hydroxylactone (structure **2** with the olefinic linkage saturated, $C_{15}H_{24}N_2O_7$; mp 247–248° dec; $\nu_{\max}^{\mathrm{KBr}}$ 1730 cm^{-1} (lactone C=O)) derived from **2** by sodium borohydride reduction confirms the vicinal relationship of the two hydroxyl groups in actinobolin as suggested by the product of base hydrolysis.

Evidence linking the lactone carbonyl at C-9 (structure **1**) rather than at the alternate α position, C-7, is obtained by irradiation of the H-6 signal (part of a three-proton multiplet centered at δ 5.25) in the nmr spectrum (CDCl$_3$) of pyrazolone **11**. This results in the collapse of the methylene proton (H-7) doublet at δ 3.42 to a singlet as expected.

Finally, a computer analysis[1] of the structural implications of the evidence presented reveals *no* other structure equally consistent with these data; therefore expression **1** for actinobolin is secured.

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(9) NASA Trainee, 1965–1967.

(10) Research Laboratories, Parke Davis and Co., Ann Arbor, Mich.

Morton E. Munk, Denny B. Nelson, Frederick J. Antosz[9]
Delbert L. Herald, Jr., Theodore H. Haskell[10]
Department of Chemistry, Arizona State University
Tempe, Arizona 85281

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Triphenylphosphine Complexes of Ruthenium and Rhodium. Reversible Combinations of Molecular Nitrogen and Hydrogen with the Ruthenium Complex

Sir:

Preparations of tris(triphenylphosphine)cobalt complexes coordinated with molecular nitrogen and some exchange reactions of the nitrogen-coordinated complexes have been reported.[1-3] In nitrogentris(triphenylphosphine)cobalt, the N_2 ligand can be readily displaced at room temperature by gases such as hydrogen, ethylene, and ammonia but not by an inert gas like argon.[1] In the course of our study to prepare similar transition metal complexes with an ability to combine with N_2, we discovered that a triphenylphosphine–ruthenium complex combines with N_2 in a benzene solution and the coordinated N_2 ligand can be easily expelled from the ruthenium complex by passing an argon stream through the benzene solution at room temperature. Divalent ruthenium complexes coordinated with N_2 are known,[4-6] but no instance of a reversible combination of N_2 with a ruthenium complex has been reported.

The ruthenium complex was prepared from RuCl$_3$ or ruthenium(III) acetylacetonate by reduction with triethylaluminum in the presence of triphenylphosphine in tetrahydrofuran or benzene in an atmosphere of nitrogen at room temperature. The light yellow diamagnetic complex obtained was slightly soluble in benzene, toluene, and tetrahydrofuran and was recrystallized from these solvents. The complex slowly decomposes in air.

Anal. Calcd for $C_{72}H_{60}P_4Ru$: C, 75.2; H, 5.26. Calcd for $C_{72}H_{62}P_4Ru$: C, 75.1; H, 5.43. Found: C, 75.7; H, 5.53.

The low solubility of the complex in organic solvents hindered the measurement of the nmr spectrum and the molecular weight. The infrared spectrum of the solid complex (Nujol mull) shows the presence of $\nu_{\mathrm{Ru-H}}$ at 2080 cm^{-1}, which is not detectable in benzene solution. The thermal decomposition, acidolysis, and a reaction with iodine released hydrogen from the Ru complex. From these results a hydride structure must be considered. A monohydride structure $HRu(PPh_3)_4$ is not compatible with the diamagnetism of the complex, and its dimeric structure $[HRu(PPh_3)_4]_2$ appears to be improbable from a steric consideration. Therefore we tentatively propose a dihydride structure $H_2Ru(PPh_3)_4$ for the complex. However, the possibility of a σ-phenyl monohydride structure,[7-9] $HRu(PPh_3)_3(PPh_2C_6H_4)$, which may be formed by a hydrogen transfer from the *ortho* position of a phenyl group to Ru cannot be excluded.

When nitrogen is bubbled through the benzene solution of the complex at room temperature, the red color of the solution turns brownish and a sharp infrared band appears at 2143 cm^{-1}. This band disappears on passing argon through the solution at room temperature accompanied by a color change of the solution from brown to red. The cycle can be repeated many times. A part of the band at 2143 cm^{-1} was shifted to 2110 cm^{-1} when the reaction was carried out with nitrogen containing $^{29}N_2$. From these results we assign the band at 2143 cm^{-1} to the coordinated N-N stretch.[1-6] A similar reversible combination of molecular nitrogen with the ruthenium complex is observed when hydrogen or ammonia is used in place of argon. The N_2 ligand is so loosely bound to the complex that,

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so far, attempts to isolate a nitrogen-coordinated complex have failed.

The addition of excess triphenylphosphine to the benzene solution interferes with the combination of molecular nitrogen; the more triphenylphosphine that is added to the solution, the weaker the band at 2143 cm^{-1} becomes. Probably in the benzene solution the triphenylphosphine–ruthenium complex is dissociated to free triphenylphosphine and a partly dissociated species, which can combine with N_2. The addition of triphenylphosphine may interfere with the dissociation, thus preventing the coordination of N_2 to Ru. In the case of nitrogentris(triphenylphosphine)cobalt, in which the N_2 ligand is tightly bound to cobalt, the addition of excess triphenylphosphine to the benzene solution causes no change in the intensity of the N_2 stretch band.

A similar reversible reaction of the ruthenium complex is observed with molecular hydrogen. When hydrogen gas is bubbled through the benzene solution a new broad band which is ascribable to a Ru–H stretch appears at about 1910 cm^{-1}. The band disappears when argon gas is passed through the solution and the cycle can be repeated many times.

Similarly a triphenylphosphine–rhodium complex was obtained from $RhCl_3$ or rhodium(III) acetylacetonate by reduction with triethylaluminum in the presence of triphenylphosphine. The yellow diamagnetic complex is slightly soluble in benzene and toluene and was recrystallized from toluene, mp 162–163°, $\nu_{\mathrm{Rh-H}}$ 2147 cm^{-1} (Nujol).

Anal. Calcd for $C_{72}H_{61}P_4Rh$: C, 75.0; H, 5.33. Found: C, 75.6; H, 5.54.

The complex liberates only a trace of H_2 on pyrolysis but releases about 0.4 mole of H_2 per Rh on acidolysis. It was converted to $HRh(Ph_2PC_2H_4PPh_2)_2$, $\nu_{\mathrm{Rh-H}}$ 1907 cm^{-1}, by a reaction with 1,2-bis(diphenylphosphino)ethane.[10] The complex is considered to be identical with $HRh(PPh_3)_4$ which was prepared independently by Takesada, Yamazaki, and Hagihara[11] by a hydrogenolysis of (1,5-cyclooctadiene)(triphenylphosphine)phenylrhodium.

In contrast to the triphenylphosphine–cobalt and –ruthenium complexes, no indication of the N_2 coordination to the rhodium complex was observed at room temperature and atmospheric pressure of nitrogen.

The three triphenylphosphine complexes of cobalt, ruthenium, and rhodium contrast with each other in their ability to combine with molecular nitrogen.

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Akio Yamamoto, Shoji Kitazume, Sakuji Ikeda
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, Ookayama, Meguro, Tokyo, Japan

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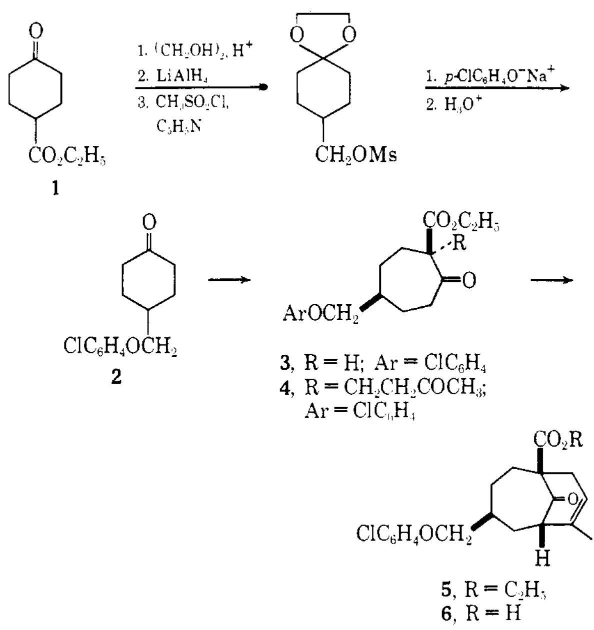
The Total Synthesis of Racemic Bulnesol

Sir:

The formidable stereochemical problems associated with the simple bicyclic guaiazulenic sesquiterpenes[1] have long thwarted attempts at complete structure elucidation and stereoselective total synthesis.[2] Thus, for example, the currently accepted structure for bulnesol (**18**), a hydroazulene with but three asymmetric centers, could be deduced only after extensive degradative studies by numerous workers.[3] In this report we describe a stereoselective total synthesis of bulnesol which fully supports the assigned structure and indicates possible solutions to some of the difficult synthesis problems associated with this class of compounds.

Keto ester **1**[4] was converted according to the scheme outlined in Chart I to 4-(*p*-chlorophenoxymethyl)-cyclohexanone (**2**) [mp 64–65°, $\lambda_{\max}^{\mathrm{KBr}}$ 5.82 (CO), 6.23, 6.30 (aromatic C=C), 6.69, 6.79, 8.52, 9.62, 12.02, and 14.95 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.97 (aromatic C-H, A_2B_2, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 24.5 Hz), and 3.81 ppm (OCH_2CH doublet, J = 6 Hz)]. Ring enlargement with ethyl diazoacetate–boron trifluoride etherate[5] afforded the β-keto ester **3** which readily condensed with methyl vinyl ketone in the presence of dilute ethanolic sodium ethoxide. The resulting diketo ester **4** cyclized upon treatment with sulfuric acid–acetic acid (4:1)[6] giving the bicyclo[4.3.1]decenone ester **5**, which was purified *via* saponification to the keto acid **6** [mp 183–185°, $\lambda_{\max}^{\mathrm{KBr}}$ 2.92–3.90 (acid OH), 5.83 (CO), 6.24, 6.31 (C=C), 6.69, 6.80, 7.78, 8.02, 12.08, and 14.95 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 9.13

Chart I



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