

Table II. Infrared Spectra of $[\text{CpCo}(\text{CO})]_3^a$

Nujol	1833, 1775, 1673
THF	1958 (s), 1843 (m), 1805 (s), 1760 (s), 1702 (m)
CHCl_3	1959 (s), 1840 (m), 1797 (m), 1750 (m), 1710 (w)
C_6H_6	1959 (s), 1811 (s), 1753 (m)

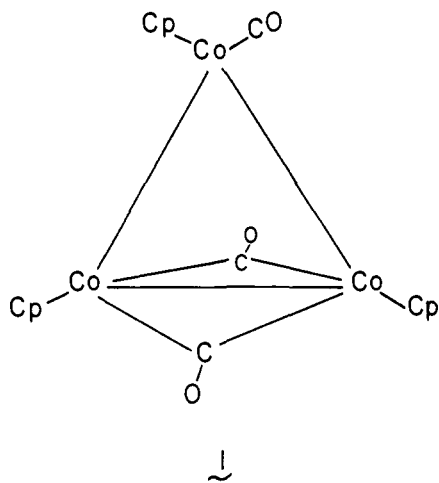
^aSpectra in cm^{-1} recorded on a Perkin-Elmer 267 spectrometer and calibrated with polystyrene

$[\text{CpCo}(\text{CO})]_3$ form an isosceles triangle with the two distinct cobalt-cobalt bond lengths of 2.521 Å (Co1-Co3) and 2.449 Å (average of Co1-Co2 and Co2-Co3). The molecule has approximate C_{2v} symmetry (though no crystallographic symmetry is imposed) with the minor plane passing through Co2, C3, O3, and bisecting the Co1-Co3 bond. Though the cobalt-cobalt bond lengths of $[\text{CpCo}(\text{CO})]_3$ vary from 2.440 to 2.521 Å, this variation is well within the range found for other reported cobalt-cobalt single bonds: 2.365 Å, $\text{Cp}_3\text{Co}_3(\mu_3\text{-CO})(\mu_3\text{-O})$;⁶ 2.463 Å, (*t*-Bu₂-C₂)Co₂(CO)₆;⁹ and 2.457–2.527 Å, Co₄(CO)₁₂.¹⁰

The solid-state infrared spectrum of $[\text{CpCo}(\text{CO})]_3$, 1833, 1775, and 1673 cm^{-1} , (cf. 1835, 1775, and 1675 cm^{-1} reported by Vollhardt et al.⁷) is readily interpreted in terms of the structure reported here. The 1673- cm^{-1} band is assigned to the C-O stretch of the triply bridging CO while the 1833- and 1775- cm^{-1} bands can be assigned to symmetric and antisymmetric stretching modes of the semibridging CO's. The solid-state infrared spectrum is somewhat dependent upon what solvent was used for crystallization in that peaks corresponding to King's "second isomer" may or may not be present. However, we feel that in light of the apparent ease with which the positions of the CO ligands can be changed, *vide infra*, this "second isomer" is basically the same as the structure reported here but with only slight changes in the three CO positions.

Infrared spectra of $[\text{CpCo}(\text{CO})]_3$ recorded in solution are vastly different and vary markedly from one solvent to another, as shown in Table II.

For example, in benzene the infrared spectrum of $[\text{CpCo}(\text{CO})]_3$ exhibits three bands: 1959, 1811, and 1753 cm^{-1} . These bands are indicative of structure **1**, whose rhodium



analogue¹¹ has been characterized by x-ray crystallography and infrared spectroscopy (KBr: 1973, 1827, 1794, and 1744 cm^{-1}). Furthermore the infrared spectra (both in solution and in the solid state) of the methylcyclopentadienyl analogue, $[\text{Me-Cp}]\text{Co}(\text{CO})_3$, exhibits three bands at 1957 ± 4 , 1843 ± 5 , and 1800 ± 6 cm^{-1} which are again consistent with **1**.

It appears that the geometry of the three CO ligands relative to the central triangle of metal atoms in complexes of the type, $[\text{CpM}(\text{CO})]_3$ (M = Co, Rh^{11,12}), is very sensitive

to subtle changes in the environment of the molecule (e.g., solid state vs. solution, polarity of solvent, etc.). We propose that molecules of such extraordinary deformability or plasticity be designated *ficile* molecules.

Further chemical, spectroscopic, and structural studies on this and related systems are now in progress. A full account of the structure of $[\text{CpCo}(\text{CO})]_3$ together with the results of all of our spectroscopic and chemical studies will be the subject of a future paper.¹³

References and Notes

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Nonspecific Biosynthesis of Hopane Triterpenes in a Cell-Free System from *Acetobacter rancens*

Sir:

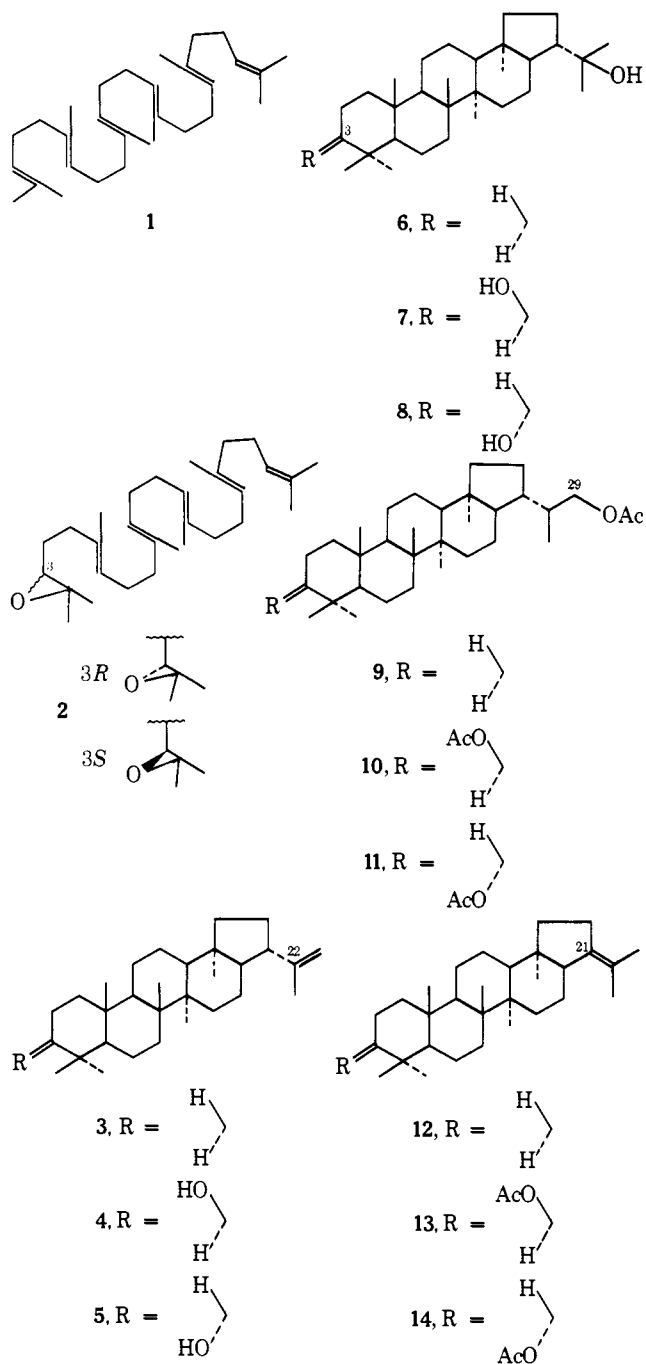
3-Desoxytriterpenes of the hopane family are ubiquitous constituents of sedimentary organic matter (including petroleum, coals, shales, muds, etc.).¹ They are also present in many procaryotic microorganisms, blue-green algae or bacteria.² We have studied one aspect of their biosynthesis, namely, the use of a cell-free system derived from an *Acetobacter*; this has revealed a novel type of enzyme-mediated reaction, with an unusually low degree of substrate selectivity but a high degree of product specificity.

The immediate precursor of 3-desoxytriterpenes has been shown in two instances to be squalene **1**, and not squalene 2,3-epoxide **2**; this is the course of the biosynthesis of tetrahymanol in a protozoan, *Tetrahymanol pyriformis*,³ and of the biosynthesis of fern-7-ene in a fern, *Polypodium vulgare*.⁴

We have therefore incubated $[12,13\text{-}^3\text{H}]$ squalene (6×10^6 dpm) with a system obtained from cells of *Acetobacter rancens* (strain NCIM 6249), disrupted by ultrasound treatment in a phosphate buffer (pH 7.4).

The expected cyclization products, hop-22(29)-ene (**3**) and hopan-22-ol (**6**), were added as carriers to the organic extract and reisolated by thin-layer chromatography on silica gel. Constant specific radioactivity was achieved after one recrystallization, and maintained through three more.

The two substances identified in this way were furthermore converted to derivatives. Hop-22(29)-ene **3** gave 29-acetoxyhopane **9** by hydroboration, oxidation with hydrogen peroxide, and acetylation; hopan-22-ol **6** gave hop-21-ene **12** by dehydration with phosphorus oxychloride and pyridine. These two derivatives were themselves purified to constant specific radioactivity, reached after one recrystallization and maintained through three more.



This demonstrates the expected incorporation of squalene into hopane derivatives; the yield of conversion (certainly not the best attainable) is ca. 6%: 3% into each of the products.

When [12,13-³H]-(3*R,S*)-oxidosqualene **2** was incubated with the same enzyme system under the same conditions, as expected, radioactive cycloartenol and lanosterol were not detected. This is in accord with the absence of detectable amounts of sterols in *Acetobacter*. However, *unexpectedly*, four new labeled metabolites, absent from the normal lipid fraction of *Acetobacter*, were isolated. These were characterized as the 3-hydroxyhopane derivatives **4**, **5**, **7**, and **8** by recrystallization to constant specific radioactivity, with authentic samples. The products **4** and **5** were acetylated, and compounds **7** and **8** were converted to **13** and **14** obtained by dehydration of the monoacetates of **7** and **8**. The respective products retained their specific radioactivity at a constant level on multiple recrystallizations. The acetates of **4** and **5** were converted into the 29-acetoxy derivatives **10** and **11** and crystallized to constant specific radioac-

tivity.

This proves that the enzyme system responsible, in *A. rancens*, for the cyclization of squalene itself is also able to cyclize the unnatural substrate, squalene epoxide, to give products differing from the normal ones only by the additional presence of a 3-hydroxy group. Furthermore, whereas eucaryotic cells cyclize only (3*S*)-squalene epoxide and leave the (3*R*) enantiomer intact,⁵ the enzyme system of *A. rancens* forms 3β-hydroxyhopane derivatives from the (3*S*) enantiomer, and their 3α-isomers from the (3*R*) enantiomer.⁶ The conversion of **2** is ca. 3% into the 3β- and 2% into the 3α-epimers.

The prokaryotic squalene cyclase of *Acetobacter rancens* is therefore "primitive" in that it displays a remarkable lack of substrate specificity at the site of initiation (acidic) of the cyclization. This indicates that the absence of 3β-hydroxytriterpenes in this microorganism (and in many others)⁷ is due to the absence of squalene epoxide.⁸

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Base-Promoted Hydrolysis of Amides at Ambient Temperatures

Sir:

Often one is presented with the problem of hydrolyzing amides which are acid sensitive and thermally labile. The obvious method for use in such situations would be hydrolysis with base. However, base hydrolysis of amides is frequently an inefficient process. While addition of hydroxide ion to an amide of general formula **1** should occur with relative ease to produce **2**, the thermodynamically preferred route for the breakdown of **2** involves loss of hydroxide to regenerate **1**.¹⁻³ In principle, if the hydroxylic proton of **2** could be removed by a second strong base, **3** should be generated.^{4,5} Cleavage of **3** with loss of amide anion would generate **4** and **5**. We now wish to report that we have developed reaction conditions which promote this transformation at room temperature.

