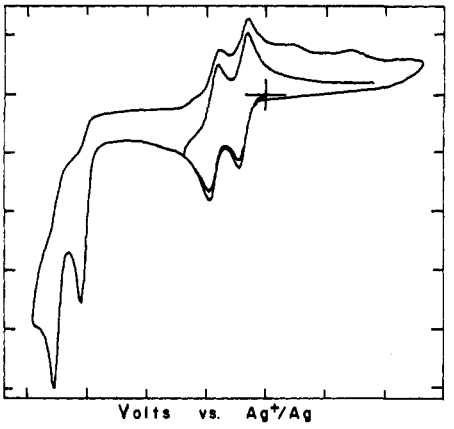

Figure 1. Cyclic voltammogram of 0.87×10^{-3} *M* **3** in 0.05 *M* TEAP, CH_3CN, Pt electrode (0.215 cm^2), 0.104 V/sec: abcissa, volts *vs.* Ag^+/Ag, 0.5 V/div; ordinate, 25 μA/div; the cross marks the (0,0) point.

respond to the formation of the radical cation and dication of **3**, respectively. The deep pink solution of the radical cation is stable for an extended period of time, while the dication, which is deep blue in solution, is stable only in the absence of oxygen and water. Spectral data are given in Table I; however, uv data below 300 nm could not be obtained for the dication since solvent impurities decomposed the dication when the solution was diluted. The esr spectrum of the radical cation exhibited unresolved hyperfine structure superimposed on an intense absorption. Seven lines could be discerned in the second derivative spectrum (splitting ≈ 0.24 G, $g = 2.00764$).

Two irreversible two-electron waves at 1.78 and 2.00 V *vs.* sce (E peak values) are observed in the voltammograms of **3** (Figure 1). No evidence of a radical trication species is present in the voltammograms at sweep rates up to 200 V/sec. The electrochemical behavior of **3** and the synthetic intermediates and the reactions of **3** with electron acceptors are under investigation and will be reported in due course.

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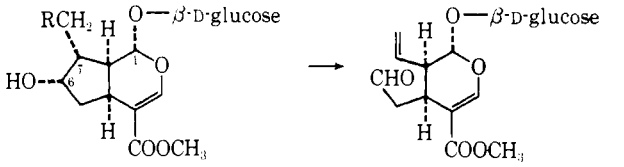
Fragmentation of Hydroxyloganin Derivatives. An Easy Access to Secologanin Type Compounds

Sir:

Secologanin (**3**), a naturally occurring monoterpene glucoside, is a key intermediate in the biogenesis of *Corynanthe*, *Aspidosperma*, and *Iboga*,[1] as well as *Ipecacuanha*[2] and *Cinchona*[3] alkaloids.

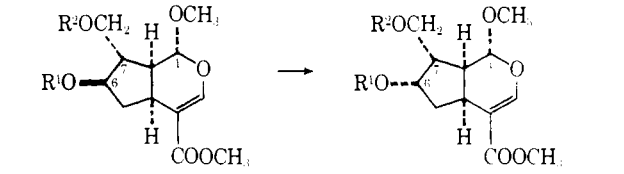
We now wish to report a simple synthesis of secologanin derivatives, which is not only fascinating from the biogenetic standpoint but also offers an easy entry to a great number of pharmacologically interesting compounds.

It has been shown by feeding experiments[1] that *in vivo* secologanin (**3**) derives from loganin (**1**) by cleavage

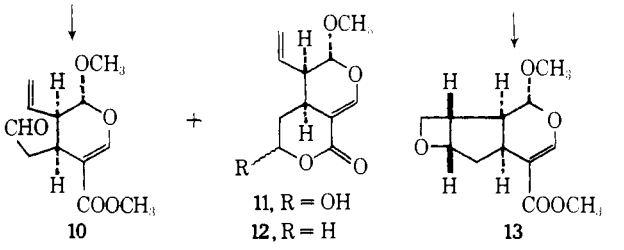


of the carbocyclic ring. Two mechanisms have been considered: (a) direct fragmentation of loganin (**1**) by hydride abstraction;[4] (b) fragmentation of the postulated intermediate hydroxyloganin (**2**). According to this, we investigated the fragmentation[5] of derivatives of hydroxyloganin, and hereby we could show that the base-catalyzed reaction of **6** leads to compounds of secologanin in high yield.

Conversion of the hydroxy acetate **4**[6] into the crystal-



4, $R^1 = COCH_3$; $R^2 = H$
5, $R^1 = COCH_3$; $R^2 = SO_2C_6H_4CH_3$-*p*
6, $R^1 = H$; $R^2 = SO_2C_6H_4CH_3$-*p*
7, $R^1 = R^2 = COCH_3$
8, $R^1 = R^2 = H$
9, $R^1 = H$; $R^2 = SO_2C_6H_4CH_3$-*p*



line *p*-toluenesulfonate **5** (mp 90–91°) (TsCl, pyridine, 20°) and hydrolysis of the acetoxy group by barium hydroxide in anhydrous methanol at 20° afforded **6** (88%). Herein the substituents at C-6 and C-7 have trans configuration. Reaction of **6** with *n*-butyllithium or potassium *tert*-butoxide did not produce any of the desired compound, whereas the reaction with sodium methylsulfinylmethide[7] in dimethyl sulfoxide at 20° gave the secologanin aglucone *O*-methyl ether (**10**) (nmr ($CDCl_3$) δ 9.78 (t, 1, J = 2 Hz, $-CHO$), 7.52 (d, 1, J = 2 Hz, $C{=}CHO$), 5.8–5.1 (m, 3, $-CH{=}CH_2$), 4.83 (d, 1, J = 4.5 Hz, $OCHO$), 3.70 (s, 3, $-CO_2CH_3$), 3.50 (s, 3, $-OCH_3$); mass spectrum *m/e* 240 (M^+)) and the lactol of the secologanic acid aglucone *O*-

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(2) A. R. Battersby and R. J. Parry, *Chem. Commun.*, 901 (1971); A. R. Battersby and B. Gregory, *ibid.*, 134 (1968).
(3) A. R. Battersby and R. J. Parry, *Chem. Commun.*, **30**, 31 (1971); A. R. Battersby and E. S. Hall, *ibid.*, 194 (1970).
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(5) H. B. Henbest and B. B. Millward, *J. Chem. Soc.*, 3575 (1960); O. Kovács, J. Szilágyi, and G. Schneider, *Magy. Kem. Foly.*, **71**, 93 (1965).
(6) L.-F. Tietze, *Angew. Chem., Int. Ed. Engl.*, **12**, 853 (1973).
(7) E. J. Corey, R. B. Mitra, and H. Uda, *J. Amer. Chem. Soc.*, **86**, 485 (1964).

methyl ether (**11**) (mp 116–117°; nmr ($CDCl_3$) δ 7.67 (d, 1, J = 2 Hz, C=C*H*O), 6.35 (broad s, 1, exchanges with D_2O), 5.9–5.1 (m, 4, -C*H*=CH_2 and HOC*H*O), 4.92 (d, 1, J = 3 Hz, OC*H*O), 3.50 (s, 3, -OCH_3); mass spectrum m/e 226 (M^+)). The product ratio depends on the reaction time and the amount of base used. A fourfold excess of the base and a reaction time of 20 sec led to **10** in 67% yield (only a trace of **11** was found) while a 2.5-fold excess and 120 sec gave a mixture of **10** (40%) and **11** (47%). Reduction of **11** with excess sodium borohydride at 20° in methanol afforded after distillation sweroside aglucone *O*-methyl ether (**12**): bp 105° (bath) (0.01 mm); nmr ($CDCl_3$) δ 7.67 (d, 1, J = 2 Hz, C=C*H*O), 5.1–5.8 (m, 3, -C*H*=CH_2), 4.91 (d, 1, J = 2 Hz, OC*H*O), 4.6–4.1 (m, 2, CCH_2O), 3.50 (s, 3, -OCH_3); mass spectrum m/e 210 (M^+).

In order to investigate the fragmentation of the *p*-toluenesulfonate of the cis 1,3-diol, we converted **4** into the diacetate **7**.[6] Hydrolysis to the diol **8** ($Ba(OH)_2$, anhydrous MeOH, 20°, 96%) and selective tosylation of the primary hydroxy group gave **9** (TsCl, pyridine, 8°, 92%), in which the same stereochemistry is present as in natural loganin (**1**). Treatment of **9** with various bases gave neither fragmentation nor elimination but by intramolecular nucleophilic substitution only an oxetane **13**:[8] nmr ($CDCl_3$) δ 5.24 (d of d, 1, J = 5, 5 Hz, -C*H*O), 4.84 (d of d, 1, J = 7, 6 Hz, -C*H*O), 4.17 (d of d, 1, J = 6, 4 Hz, -C*H*O); mass spectrum m/e 240 (M^+). The yield was over 95% using sodium methylsulfinylmethide in dimethyl sulfoxide or potassium *tert*-butoxide in *tert*-butyl alcohol as base at 20° for 120 sec.

These results show that the postulated biogenetic pathway of secologanin (**3**) *via* hydroxyloganin (**2**) with cis orientated substituents at C-6 and C-7 is at least not realizable *in vitro*. The biogenetic significance of 6-*epi*-hydroxyloganin with trans orientated substituents at C-6 and C-7 in **2** is currently under investigation.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

(8) In some cases oxetanes can be cleaved regiospecifically to alkenes and aldehydes, see G. Jones II, S. B. Schwartz, and M. T. Marton, *J. Chem. Soc., Chem. Commun.*, 374 (1973).

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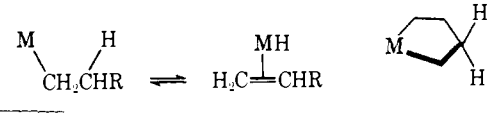
Preparation and Reactions of a Titanium(IV) Metallocycle. Formation of Cyclopentanone from Ethylene and Carbon Monoxide[1]

Sir:

The chemistry of transition metal alkyls is dominated by the (frequently reversible) β elimination of metal hydrides. We recently established that the rate of



platinum(II) hydride elimination from tetra- and pentamethylenebis(*tert*-phosphine)platinum(II) complexes is strongly inhibited relative to that of acyclic analogs, presumably as a result of the inability of the metallocyclic complexes to achieve the 0° M–C–C–H dihedral angle most favorable for metal hydride elimination.[2] If an unusually slow rate of metal hydride elimination were to prove a general characteristic of metallocycles, these compounds might display unusual types of reactions, normally masked by the hydride elimination in analogous acyclic organometallics. Here we wish to report the synthesis of a new metallocycle, dicyclopentadienyltetramethylenetitanium(IV) (**1**), and to describe several reactions of this substance that do not have close analogy in the chemistry of similar acyclic titanium(IV) alkyls.

Reaction of Cp_2TiCl_2 with 1,4-dilithiobutane in diethyl ether at −78° yields **1**.[3] This compound is stable only below −30°; its purification was accomplished by removal of ether from the reaction mixture under vacuum, extraction of the residue with pentane, and chromatography of the pentane extract on Woelm Activity I alumina. All operations were performed below −40° under nitrogen or argon. Compound **1** was obtained as a bright orange solid; its yield was ~20% based on Cp_2TiCl_2, as determined by proteolysis to butane or bromination to 1,4-dibromobutane (*vide infra*). It can be recrystallized with difficulty from pentane at −100°; the properties of **1** before and after recrystallization are indistinguishable.

Elemental analysis of **1** is precluded by its thermal instability. Its solubility is sufficient to show a resonance due to the Cp protons as a sharp singlet in the nmr spectrum at δ 6.20 (CF_2ClCCl_2F); the methylene region of the spectrum is obscured by residual ether and pentane from its preparation. Its structural assignment rests on the reactions outlined in Scheme I. Reactions of **1** with HCl or bromine yield the expected butane or 1,4-dibromobutane; these reactions are assumed to proceed in high yield and provide our method of assay for **1** in solutions following chromatographic purification. Carbonylation of **1** at −40° in Et_2O (CO pressure = 10 atm), followed by gradual warming of the reaction mixture to room temperature over several hours, generates cyclopentanone in 80% yield.[4] Careful reaction of a pentane solution of **1** with carbon monoxide (1 atm) at −78° for 1 hr precipitates compound **2** as a bright yellow solid in 75% yield; this substance is assigned the structure of a carbon monoxide insertion product on the basis of ir (C=O stretch at 1730 cm^{-1}) and nmr (CD_2Cl_2) δ 6.25 (s, 10 H, Cp), 1.0–2.5 (m, 8, $(CH_2)_4$). Compound **2** can be recrystallized from toluene at low temperature. It decomposes at room temperature on standing as a solid or in solution; its half-life in CH_2Cl_2 is ~15 min at 35°. When **2** is heated briefly in toluene to 70°, cyclopentanone is generated as the major volatile product.

The chemistry of **1** contrasts markedly with that of an acyclic analog, Cp_2TiBu_2 (**3**), in several respects.

(1) Supported by the National Science Foundation, Grant No. GP-28586X.

(2) J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **95**, 4451 (1973).

(3) Similar preparations have been employed for $Cp_2Ti(CH_3)_2$ [K. Claus and G. Bestian, *Ann. Chem.*, **654**, 8 (1962)] and $Cp_2Ti(CH_2Ph)_2$ [H. J. deLiefde Meijer and F. Jellineck, *Inorg. Chim. Acta*, **4**, 651 (1970)].

(4) $Cp_2Ti(CH_2Ph)_2$ has been converted to dibenzyl ketone on carbonylation: G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 654 (1972).