$$Rh(NO)L_3 + PhCOCl \longrightarrow \underset{\mathbf{3a}}{Rh(NO)(PhCO)ClL_2} + L$$

$$\mathbf{3a} \xrightarrow{THF,\ 25^\circ} \mathbf{3b}$$

$$\mathbf{3b} \xrightarrow[60^\circ]{THF} \underset{\mathbf{4}}{Rh(CO)ClL_2} + L$$

After 8 days in THF, **3a** is converted into a poorly characterized brown crystalline complex, **3b**, whose ir spectrum shows the absence of a benzoyl group and the presence of a carbonyl and a nitrosyl group (Table I). Heating the benzoyl adduct in THF affords the known rhodium carbonyl **4**, probably by way of **3b**. The fate of the other products has not been determined.

Table I. Infrared Spectra

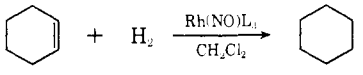
Compound	γ_{NO}(KBr), cm^{-1}	Misc
$Rh(NO)L_3$ (**1a**)	1610	
$Ir(NO)L_3$ (**1b**)	1600	
$Rh(NO)I_2L_2$ (**2**)	1628	
$Rh(NO)PhCO)ClL_2$ (**3a**)	1608	1660, 860 (PhCO)
Rh(NO)(CO)(Ph)ClL (**3b**)	1630	1970 (CO), 338 (Rh–Cl)
$Rh(NOH)Cl_3L_2$ (**5a**)		3330, 3230 (OH?)
		2470, 2380 (OD?)
$Rh(HNO)Cl_3L_2$ (**5b**)	1638	3280, 3230 (NH?)
		2460, 2380 (ND?)

Dry HCl reacts with **1a** to form a mixture of two apparently tautomeric adducts **5a** and **5b**. Three equiv-

$$Rh(NO)L_3 + 3HCl \longrightarrow \underset{\mathbf{5a}}{Rh(NOH)Cl_3L_2} + \underset{\mathbf{5b}}{Rh(HNO)Cl_3L_2}$$

alents of HCl is consumed and H_2 is evolved, but in low (9%) yield (vacuum line and vpc analysis). The less soluble yellow adduct **5a**, which occluded solvents and proved difficult to purify, was transformed into the orange isomer **5b** by treatment with methanol. The dichloride, $RhCl_2(NO)L_2$, does not react with HCl under these conditions, even though Roper found $IrCl_2(NO)L_2$ to be the product of HCl addition to **1b**. The ir spectra of **5a** and **5b** support our supposition that these may be tautomeric complexes of the unknown nitroxyl. Both exhibit NH or OH bands (Table I) which are appropriately shifted when DCl is used. The yellow isomer **5a** lacks a band attributable to an NO group, but **5b** exhibits an NO band at 1635 cm^{-1}.

The rhodium nitrosyl **1a** does not form a stable adduct with H_2 as judged from the constancy of its uv-visible and ir spectra under a H_2 atmosphere. Nevertheless, **1a** effectively catalyzes the hydrogenation of terminal and cyclic olefins.



1-Hexene and cyclohexene are quantitatively reduced in CH_2Cl_2 solutions at 25° and 55 psi (or 1 atm). If peroxide-free olefins are used in an O_2-free environment, olefin isomerism does not take place and the catalyst can be recovered unchanged. Triphenylphosphine retards these hydrogenations. It is perhaps significant that a formally d^{10} complex activates hydrogen. Under the same conditions, the iridium analog **1b** fails to catalyze these reactions; however, in benzene at 85° **1b** does catalyze the reduction of 1-hexene with isomerization.

Treatment of cyclohexene with D_2 in the presence of **1a** afforded $C_6H_{10}D_2$ in >99% isotopic purity (mass spectral analysis), suggesting that this catalyst will prove to be stereospecific. Only one other compound,[11] RhL_3Cl, is reported to catalyze deuteration without H, D scrambling. Further studies on the use of **1a** in catalysis and the mechanism of these reactions are continuing.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 9101) and the Center for Materials Research at Stanford University for support which made this research possible.

(11) J. A. Osborn, F. H. Jardine, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1968).

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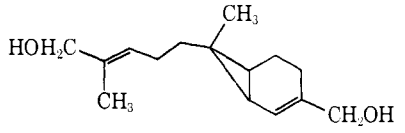
The Total Synthesis of *dl*-Sirenin

Sir:

The structure I has recently been established for sirenin, the sperm attractant produced by the female gametes of the water mold, *Allomyces*.[1-4] We were drawn to the problem of synthesizing it because it appeared that the intramolecular addition of olefinic diazo ketones which was introduced some years ago[5] should be a particularly suitable method for the stereospecific construction of the sirenin molecule, *e.g.*, *via* II. Furthermore, the unsaturated acid needed as a precursor of II (*cf.* VI, R = OH) could obviously be made easily by procedures which we had developed in another connection.[6]



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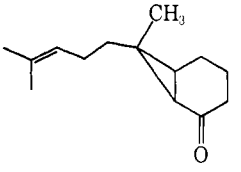
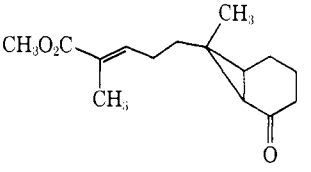


II

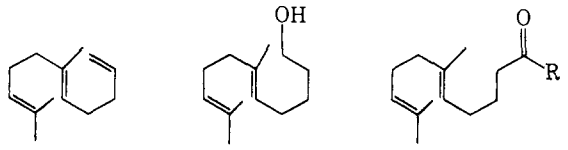


III

Treatment of geranyl chloride (in ether–HMPA) with excess allylmagnesium bromide in ether by the general method previously described[6] produced the triene

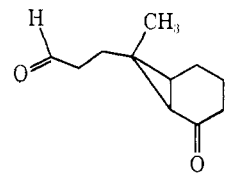
(1) L. Machlis, *Physiol. Plant.*, 11, 181 (1958).
(2) L. Machlis, W. H. Nutting, M. W. Williams, and H. Rapoport, *Biochemistry*, 5, 2147 (1966).
(3) L. Machlis, W. H. Nutting, and H. Rapoport, *J. Amer. Chem. Soc.*, 90, 1674 (1968).
(4) W. H. Nutting, H. Rapoport, and L. Machlis, *ibid.*, 90, 6434 (1968).
(5) G. Stork and J. Ficini, *ibid.*, 83, 4678 (1961). This method is especially useful in the construction of II because of the stereospecific nature of ketocarbene additions; *cf.* G. Stork and M. Gregson, *ibid.*, 91, 2373 (1969), footnote 6.
(6) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Lett.*, 1393 (1969). The geranyl chloride, bp 64–65° (0.5 mm) (incorrectly reported as 64–65° (0.05 mm) by Stork), was made from pure geraniol obtained from geraniol "Palma Rosa" through the courtesy of International Flavors and Fragrances.

IV in >90% yield: bp 80–81° (~10 mm); λ^{film} 6.05, 10.95 μ. The nmr (CCl_4) showed the expected ABX pattern of the terminal vinyl group around δ 5 and the mass spectrum exhibited a molecular ion at *m/e* 178. Tlc (hexane) and glpc (SE 30, 165°, 10 ft × 0.25 in., 100 ml/min, retention time 4.5 min) showed the triene to be homogeneous. Hydroboration using disiamylborane, followed by the usual oxidation ($NaOH-H_2O_2$), produced the primary alcohol V [bp 104–105° (~0.8 mm); λ^{film} 3300 cm^{-1}; δ (CCl_4) 3.54 (t, $J \sim 6$, 2 H), 5.11 (t, broad, 2 H)] in 70% yield. Jones oxidation of alcohol V (inverse addition at 0°) produced in 70% yield the corresponding acid VI, R = OH; bp 135–145° (~0.5–0.6 mm); λ^{film} 5.82 μ; δ (CCl_4) 10.95 (s, 1 H). Treatment of an ethereal solution of the acid with diazomethane afforded its methyl ester VI, R = OCH_3, homogeneous on glpc (SE 30, 170°, 10 ft × 0.25 in., 100 ml/min, retention time 18 min); λ^{film} 5.74 μ; δ (CCl_4) 3.60 (s, 3 H). The mass spectrum showed the expected *m/e* 224. The acid VI, R = OH, was now

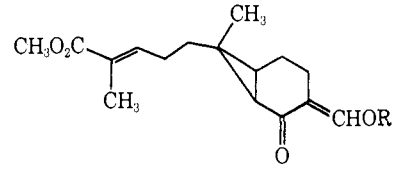


IV V VI

converted to the cyclohexanone II with a fused cyclopropane ring. Treatment of VI, R = OH, with 3 equiv of thionyl chloride and 1.5 equiv of pyridine in ether (0°–room temperature), followed by removal of solvent and excess thionyl chloride on the rotary evaporator, addition of hexane, and filtration, gave a solution of the acid chloride (λ^{film} 5.53 μ) which was added to excess diazomethane in ether to give the diazo ketone VI, R = CHN_2: λ^{film} 3.28, 4.75, 6.07 μ. The latter (Cu bronze–cyclohexane; 7-hr reflux) gave the desired II[7] in an over-all yield of 55% from the acid VI, R = OH. Chromatography on silica gel (benzene followed by benzene–ethyl acetate, 9:1) provided a pure sample of II homogeneous by glpc (SE 30, 200°, 10 ft × 0.25 in., 100 ml/min, retention time 11 min) and tlc (benzene–ethyl acetate, 9:1). Spectral data exhibited λ^{film} 5.91 μ; δ (CCl_4) 1.12 (s, 3 H), 5.11 (t, broad, 1 H); mass spectrum, *m/e* 206. Ozonolysis of II (−78°, methylene chloride) followed by treatment with dimethyl sulfide produced (90% yield) the aldehyde VIII: [λ^{film} 3.68, 5.80, 5.91 μ; δ (CCl_4) 9.80 (s, 1 H), 1.12 (s, 3 H)] which was treated with the sodium salt of methyl 2-diethylphosphonopropionate to produce in 60% yield, and apparently stereoselectively (92% *trans*), the desired *trans* compound III [λ^{film} 5.83, 5.91, 6.05 μ; δ (CCl_4) 6.62 (t, broad, 1 H), 3.66 (s, 3 H), 1.82 (s, broad, 3 H), 1.12 (s, 3 H)]. The mass spectrum showed *m/e* 250. In addition III was homogeneous on tlc (silica gel, ether–hexane 2:3 or ethyl acetate–benzene 3:17). Treatment of ketone III with 1 equiv of sodium hydride in dry dimethoxyethane (under nitrogen) and excess methyl formate (dried over K_2CO_3 and distilled from P_2O_5) at 25° for 4 hr yielded the formyl ketone VIII, R = H: λ^{film} 2.80–4.10, 5.83, 6.06–6.32 μ; δ (CCl_4) 6.62 (t, broad, 1 H), 8.25 (s, 1 H), 3.65 (s, 3 H), 1.82 (s, broad,

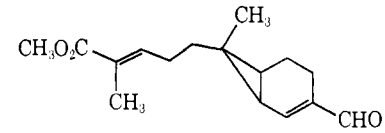


VII



VIII

3 H), 1.05 (s, 3 H). O-Alkylation was achieved in 70% yield by refluxing the sodium salt of VIII, R = H, with an excess of isopropyl iodide 2 hr in 5:2 THF–HMPA followed by chromatography on silica gel (hexane–ether 2:3). The ether VIII, R = *i*-C_3H_7, was homogeneous on tlc (silica gel, hexane–ether 2:3) and exhibited the following spectral data: λ^{film} 5.83, 5.95, 6.26 μ; δ (CCl_4) 1.05 (s, 3 H), 1.25 (d, 6 H), 1.82 (s, broad, 3 H), 3.66 (s, 3 H) 4.20 (m, 1 H), 6.62 (t, broad, 1 H), 7.20 (s, broad, 1 H). Treatment of VIII,



IX

R = *i*-Pr, with $NaBH_4$–NaOH at room temperature and subsequent hydrolysis of the crude product with 3 *N* HCl gave, after chromatography on silica gel with 3:2 ether–hexane, the α,β-unsaturated aldehyde IX (~60% yield), homogeneous on tlc (3:2 ether–hexane): λ^{film} 3.70, 5.83, 5.94, 6.03, 6.10 μ; δ (CCl_4) 0.90 (s, 3 H), 6.90 (broad, 1 H), 6.62 (t, broad, 1 H) 9.40 (s, 1 H); λ_{max}^{EtOH} 220 (ϵ 13,600), 263 mμ (ϵ 11,300).

Reduction of IX with lithium aluminum hydride in ether afforded *dl*-sirenin isolated by preparative tlc (silica gel; 4:1 ether–hexane). The *dl*-sirenin was homogeneous when resubmitted to tlc (silica gel; 4:1 ether–hexane) and showed *m/e* 236; λ^{CHCl_3} 3600, 1660, 1601, 1380, 990 cm^{-1}; δ ($CDCl_3$) 0.90 (s, 3 H), 1.67 (s, broad, 3 H), 3.95 (s, broad, 4 H), 5.36 (t, broad, 1 H), 5.80 (s, broad, 1 H).

The nmr and ir spectra were in agreement with those obtained from the natural substance.[8–10]

Acknowledgment. We thank Professor G. Stork for many helpful discussions during the course of this investigation.

(7) A synthesis of this substance has just been published: E. J. Corey and K. Achiwz, *Tetrahedron Lett.*, 1837 (1969). The method used by these authors also employs the internal diazo ketone addition.[5]

(8) We thank Professor H. Rapoport for allowing us to see these spectra.

(9) Biological tests on the synthetic material were kindly performed by Professor L. Machlis. They showed activity qualitatively identical with that of the natural material. The synthetic sample showed, however, only a quarter to a half of the activity of the natural product, possibly because unforeseen testing difficulties caused considerable delay before our sample could be assayed.

(10) This work was supported, in part, by the National Institutes of Health.

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