ethanol in the photochemical reaction of nortricyclanone and related compounds.[15]

In conclusion, an appropriate substitution of cyclopropenes with an alkylthio group permits a facile ring opening leading to indene and/or butadiene derivatives in good yields. Further studies on the reactions of 1 as well as other heteroatom-substituted cyclopropenes with various nucleophiles such as organolithium compounds, amines, and thiols are currently in progress.

(15) Yates, P. *Pure Appl. Chem.* **1968**, *16*, 93. We are indebted to a referee for calling our attention to this reference.

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New Functions of (Arene)tricarbonylchromium(0) Complexes as Hydrogenation Catalysts: Stereospecific Semihydrogenation of Alkynes and Highly Chemoselective Hydrogenation of α,β-Unsaturated Carbonyl Compounds[1]

Summary: An impressive stereo- and chemoselective catalytic hydrogenation procedure for alkynes to (*Z*)-alkenes) and α,β-unsaturated carbonyl compounds (to the saturated analogues) using (arene)$Cr(CO)_3$ catalysts is described.

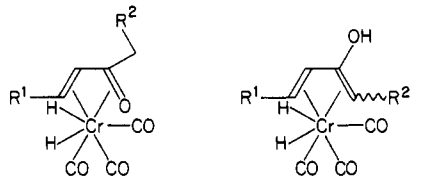
Sir: We report here that (arene)tricarbonylchromium(0) complexes, originally known as catalysts for the 1,4-hydrogenation of conjugated dienes,[2] serve as extremely useful catalysts for the hydrogenation of multiple bonds such as alkynes to (*Z*)-alkenes and α,β-unsaturated carbonyl compounds to saturated analogues. It appears that these catalysts are superior in the stereo- and chemoselectivity to ordinary catalysts including the Lindlar catalyst,[3] cationic rhodium complexes,[4] nickel boride catalysts,[5] and so on.

As shown in Table I, 1-phenyl-1-propyne (**1**) was stereospecifically hydrogenated to (*Z*)-β-methystyrene (**2**) by using the (arene)tricarbonylchromium(0) complexes as hydrogenation catalysts in very high yield (entries 1,2). Neither (*E*)-β-methylstyrene nor *n*-propylbenzene was detected by the GLC analysis of the crude reaction mixture in both cases. In contrast to the semihydrogenation of alkynes using ordinary catalysts mentioned above, even after prolonged reaction time, neither the overreduced product nor the *E* isomer was formed in the present partial hydrogenation reaction, thus characterizing (arene)tricarbonylchromium(0) complexes as catalysts for the hydrogenation of alkynes to (*Z*)-alkenes.

As the reference example, 1-phenyl-1-propyne (**1**) was hydrogenated by the Lindlar catalyst in the presence of quinoline (hexane solvent, 1 kg/cm^2 of H_2 pressure, 4.5 h). In this case a mixture of (*Z*)-β-methystyrene (**2**) (83%), (*E*)-β-methylstyrene (4%), and *n*-propylbenzene (10%) was formed along with recovery of the starting material (**1**) (3%).

Other alkynes such as 7-tetradecyne (**3**) and the propargyl alcohol derivative **4** were hydrogenated to the corresponding alkenes in excellent yields (entries 3,4,5). Also in these hydrogenations, the (*Z*)-alkenes were stereospecifically obtained without formation of the overreduced products (GLC analysis).

(Arene)tricarbonylchromium(0) complexes offer another synthetically useful reaction. Namely, α,β-unsaturated carbonyl compounds are chemospecifically hydrogenated to saturated analogues in the presence of nonconjugated double bonds.[6] For example, hydrogenation of the enone **5** gave the saturated ketone **6** in nearly quantitative yield without any isomerization of the terminal double bond (entries 6, 7). In striking contrast to this result, cyclic α,β-unsaturated ketones in which the enone system is rigidly constrained to a transoid geometry, such as 2-cyclohexenone (**7**), was found to remain unchanged under the hydrogenation conditions (entry 8), suggesting that a possible mechanism for the hydrogenation of enones involves the transition state **8** rather than **9**. Based on these



8 **9**

results, next we attempted the chemospecific hydrogenation of **10** having two enone functionalities. As was expected, specific hydrogenation proceeded quite well, affording the cyclic enone **11** in essentially quantitative yield (entry 9). To the best of our knowledge, this is the first example of the chemospecific hydrogenation of the enone functionality capable of adopting a cisoid geometry in the presence of the enone system constrained to a transoid conformation. The α,β-unsaturated ester **12**, though less reactive than α,β-unsaturated ketones, was also hydrogenated to the saturated analogue **13** in nearly quantitative yield (entry 10). Likewise the β-keto ester **14** was found to undergo hydrogenation probably via the enol form to give the hydroxy ester **15** albeit in low yield (entry 11).

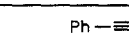
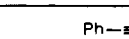
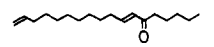
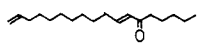
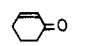
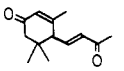
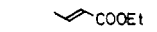
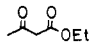
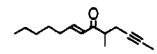
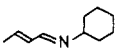
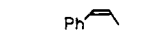
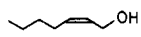
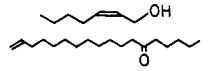
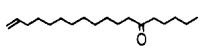
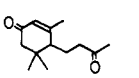
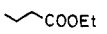
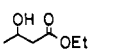
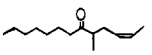
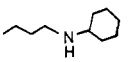
Hydrogenation of 5-methyl-6-oxo-7(*E*)-tridecen-2-yne (**16**) provided the saturated ketone **17** with the *Z* double bond stereospecificially "in a single operation" (entry 12). In the case of the α,β-unsaturated imine **18**, hydrogenation afforded the secondary amine **19** in excellent yield (entry 13).

A representative procedure follows: 1(*E*)-11-Octadecadien-13-one (**5**) (570 mg, 2.1 mmol) and naphthalenetricarbonylchromium[7] (110 mg, 0.4 mmol) was dissolved in dry THF (20 mL). After deoxygenation by three freeze–

(1) This paper is dedicated to Professor Shun-ichi Yamada on the occasion of his 70th birthday.
(2) Farona, M. F. "Organometallic Reactions and Syntheses"; Plenum Press: New York and London, 1977; Vol. 6, pp 223–288.
(3) Marvell, E. N.; Li, T. *Synthesis* **1973**, 457.
(4) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143.
(5) Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *85*, 1003. Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553. Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226.
(6) It was found that both α,β-unsaturated cyanides and α,β-unsaturated sulfones remained intact under the hydrogenation conditions. However, in the case of conjugated nitro olefins and α,β-unsaturated aldehydes, a complex mixture was obtained.
(7) Yagupsky, G; Cais, M. *Inorg. Chim. Acta* **1975**, *12*, L27. Cais, M; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27.

0022-3263/85/1950-1147$01.50/0

Table I. Hydrogenation of Alkynes, α,β-Unsaturated Carbonyl Compounds, and α,β-Unsaturated Imines

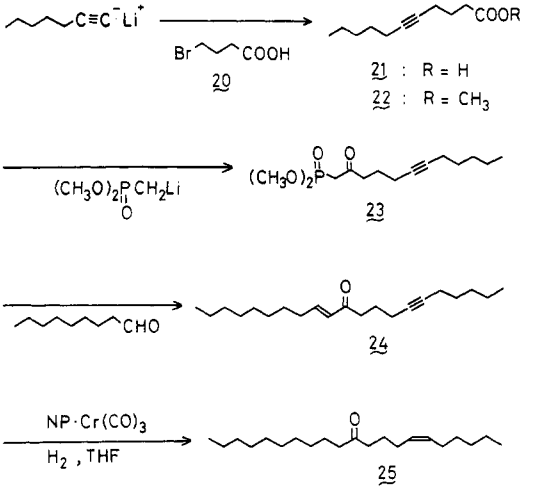
entry	starting material	no.	catalyst[a]	solvent	H_2 press., kg/cm^2	temp, °C	time, h	product	no.	yield, %
1		1	MBZ·Cr(CO)$_3$[b]	acetone	70	120	23		2	92[c]
2		1	NP·Cr(CO)$_3$[d]	THF	20	45	24		2	92[c]
3		3	MBZ·Cr(CO)$_3$	acetone	70	120	15			100[c]
4		4	MBZ·Cr(CO)$_3$	acetone	70	120	8			95[c]
5		4	NP·Cr(CO)$_3$	THF	50	45	8			87[c]
6		5	NP·Cr(CO)$_3$	THF	30	45	3		6	94[e]
7		5	MBZ·Cr(CO)$_3$	acetone	70	120	12		6	97[e]
8		7	MBZ·Cr(CO)$_3$	acetone	70	120	20	no reaction		
9		10	NP·Cr(CO)$_3$	THF	70	45	26		11	96[e]
10		12	NP·Cr(CO)$_3$	THF	95	45	30		13	99[c,f]
11		14	NP·Cr(CO)$_3$	THF	80	120	12		15	11[c,g]
12		16	MBZ·Cr(CO)$_3$	acetone	70	120	24		17	93[e]
13		18	NP·Cr(CO)$_3$	THF	70	60	19		19	90[c]

[a] In all the experiments, 0.2 molar equiv of the catalyst to the substrate was used. [b] (Methyl benzoate)tricarbonylchromium. This commercially available catalyst requires high temperature and high H_2 pressure for the hydrogenation in general. [c] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [d] Naphthalenetricarbonylchromium. The hydrogenation can proceed under the milder conditions (45 °C) in the case of this catalyst (not commercially available). The required hydrogen pressure depends on substrates. [e] Isolated yield. [f] The starting material (ca. 0.5%) was recovered. [g] The starting material (69%) was recovered.

pump–thaw cycles, the solution was transferred to an autoclave with glass insert (100 mL) and stirred for 3 h at 45 °C under 30 kg/cm^2 of hydrogen pressure. Evaporation of solvent and chromatography over silica gel using 1:30 ether–*n*-hexane for elution gave 1-octadecen-13-one (**6**) (540 mg, 94%) as a colorless solid, mp 34–36 °C.

These special characteristics of (arene)Cr(CO)$_3$ as hydrogenation catalysts were finally applied to a novel short total synthesis of (*Z*)-6-heneicosen-11-one (**25**), the principal sex pheromone of the Douglas fir tussock moth.[8,9] Retrosynthetic analysis of **25** suggested that **25** could be stereospecifically obtained from **24** by hydrogenation using an (arene)Cr(CO)$_3$ catalyst "in one step". Thus, the key intermediate **24** was first synthesized as shown in Scheme I. Treatement of the excess acetylide generated from 1-heptyne and *n*-BuLi with 4-bromobutanoic acid (**20**) afforded **21** in 43% yield based on **20**. After esterification with CH_2N_2, **22** was reacted with dimethyl α-lithiomethanephosphonate to give the ketophosphonate **23** in 96% yield. Treatment of **23** with NaH in THF followed by addition of nonanal furnished the key intermediate **24** in 88% yield. One-step transformation of **24** to the sex pheromone **25** was performed as follows: Hydrogenation of **24** by naphthalenetricarbonylchromium (183 mg/g of **24**) in degassed THF (30 mL/g of **24**) at 45 °C for 8 h (50 kg/cm^2 of H_2 pressure) provided (*Z*)-6-heneicosen-11-one

Scheme I



(**25**) with 100% stereoselectivity[10] in 88% yield. The spectral data of **25** thus obtained were identical with those reported.[8,9]

On the basis of the arguments presented above it is concluded that (arene)Cr(CO)$_3$, easily handled transition-metal complexes, are quite useful catalysts for the stereospecific semihydrogenation of alkynes to (*Z*)-alkenes as well as the highly chemoselective hydrogenation of α,β-unsaturated carbonyl compounds to saturated analogues in the presence of isolated double bonds.

(8) Smith, R. G.; Daterman, G. E.; Daves, G. D., Jr. *Science (Washington, D.C.)* **1975**, *188*, 63.

(9) For total syntheses already reported, see; Smith, R. G.; Daves, G. D., Jr.; Daterman, G. E. *J. Org. Chem.* **1975**, *40*, 1593. Kocienski, P. J.; Cernigliaro, G. J. *J. Org. Chem.* **1976**, *41*, 2927. Mori, K; Uchida, M.; Matsui, M. *Tetrahedron* **1977**, *33*, 385. Fetizon, M.; Lazare, C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 842. Ackemark, B.; Ljungqvist, A. *J. Org. Chem.* **1978**, *43*, 4387. Kondo, K.; Murahashi, S. *Tetrahedron Lett.* **1979**, 1237.

(10) Stereochemistry of the disubstituted olefin in **25** was determined by the careful NMR analysis of the corresponding epoxide (**i**). Further, both the silver nitrate impregnated TLC analysis of **25** and the GLC analysis of **i** showed none of the presence of the *E* isomer which was actually synthesized by us.

Registry No. 1, 673-32-5; 2, 766-90-5; 3, 35216-11-6; 4, 1002-36-4; 5, 95387-57-8; 6, 95387-58-9; 7, 930-68-7; 10, 79734-43-3; 11, 74233-41-3; 12, 623-70-1; 13, 105-54-4; 14, 141-97-9; 15, 5405-41-4; 16, 95387-59-0; 17, 95387-60-3; 18, 32820-47-6; 19, 10108-56-2; 20, 2623-87-2; 21, 822-02-6; 22, 54298-99-6; 23, 95387-61-4; 24, 95387-62-5; 25, 54844-65-4; 28, 124-19-6; (*Z*)-$CH_3(CH_2)_5CH$=$CH(CH_2)_5CH_3$, 41446-60-0; (*Z*)-$CH_3(CH_2)_3CH$=$CHCH_2OH$, 55454-22-3; $CH_3(CH_2)_4C{\equiv}CLi$, 42017-07-2; $(CH_3O)_2P(O)CH_2Li$, 34939-91-8; naphthalenetricarbonylchromium, 57220-00-5; 1-heptyne, 628-71-7; (methyl benzoate)tricarbonylchromium, 12125-87-0.

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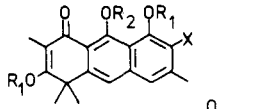
Garveatin A, an Antimicrobial 1(4*H*)-Anthracenone Derivative from the Hydroid *Garveia annulata*

Summary: The structure of garveatin A (1), an antimicrobial metabolite from the hydroid *Garveia annulata*, was inferred from its spectral data and confirmed via X-ray diffraction analysis of its triacetate 4.

Sir: Coelenterates belonging to the class Hydrozoa are small, often inconspicuous, marine invertebrates that have received very little attention from natural product chemists.[1] We report herein the structure of garveatin A (1), the major antimicrobial[2] metabolite present in the extracts of the hydroid *Garveia annulata* collected in Barkley Sound, British Columbia.

Pure garveatin A (1) (orange needles, mp 236–240 °C, acetone) was obtained by LH20 ($MeOH/CH_2Cl_2$, 9:1) and silica gel (EtOAc/hexane, 1:1) purification of the ethyl acetate soluble portion of crude methanol extracts of the hydroid. A molecular formula of $C_{20}H_{20}O_5$ was established



1 $R_1 = R_2 = H$ X = 
2 $R_1 = R_2 = Ac$ X = 
3 $R_1 = R_2 = Me$ X = 
4 $R_1 = Ac$ $R_2 = H$ X = 

by mass spectrometry (M^+ m/z obsd 340.1317, calcd 340.1311). The highly aromatic nature of garveatin A (1) was indicated by ^1H NMR ($CDCl_3$, 80 MHz) resonances at δ 7.10 (bs, 1 H) and 7.15 (s, 1 H), by its UV chromophore (MeOH, λ_{max} 232, 282, 323 (sh) and 432 nm), and by the observation of ten aromatic carbon resonances in the ^{13}C NMR ($CDCl_3$) 106.3 (s), 110.9 (s), 114.1 (d), 119.6 (d), 127.3 (s), 138.0 (s), 138.4 (s), 146.3 (s), 155.8 (s), 161.5 (s) ppm). Three additional deshielded carbon resonances at 189.3 (s), 106.7 (s), and 181.5 (s) ppm were assigned to an enolized β-diketone system which had to be alkylated at the central carbon.[3] The remaining resonances in the ^1H NMR spectrum of garveatin A (1) could be assigned to five methyl groups as follows: δ 1.63 (s, 6 H) to a pair of geminal methyls attached to a carbon which appears at 40.8 (s) in the ^{13}C NMR; 2.68 (s, 3 H) to an acetyl side chain (^{13}C NMR, 204.7 (s), 32.0 (q)); 2.40 (bs, 3 H) to an aromatic methyl; and 1.98 (s, 3 H) to the alkyl substituent on the central carbon of the β-diketone.

Garveatin A (1) forms a triacetate (2)[4] (Ac_2O, pyridine: ^1H NMR ($CDCl_3$) δ 2.35, 2.54, 2.55 all s, 3 H) which demonstrated that the three remaining protons required by the molecular formula but not observed in the ^1H NMR of 1 belonged to two phenolic and one enolic functionalities. The substituted 1(4*H*)-anthracenone derivative 1 was a biogenetically reasonable structure for garveatin A that successfully accounted for all the observed spectral data. Support for this structure came from (i) demonstration of ^1H difference NOE's between H5 and H10, between H10 and the C12 and C13 methyl protons, and between the C11 methyl and the C3 methoxy protons in the trimethoxy derivative 3, (ii) demonstration of spin coupling between H5 and the C14 methyl protons, (iii) the chemical shift of the acetyl carbonyl (δ 204.7) which requires that it be ortho to a phenol, and (iv) the similarity of the UV chromophore and the chemical shifts of H5 and H10 in garveatin A (1) and the known metabolite ferruginin A.[5]

Attempted crystallization of triacetate 2 by slow evaporation of a chloroform/hexane solution gave a 3:1 mixture of triacetates 2 and 4. We have shown that 2 can be quantitatively converted to 4 by heating with TsOH in benzene. The structure of garveatin (1) was verified by a single-crystal X-ray diffraction analysis on triacetate 4.

Preliminary X-ray photographs of garveatin A triacetate (4) displayed monoclinic symmetry. Accurate lattice constants of a = 8.1755 (15) Å, b = 18.0988 (15) Å, c = 16.0627 (22) Å, and β = 86.079 (13)° were determined from a least-squares fit of 15 diffractometer-measured 2θ values. Systematic extinctions and crystal density were uniquely accommodated by space group $P2_1/n$ with one molecule of composition $C_{26}H_{26}O_8$ as the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using variable speed, 1° ω-scans, and graphite monochromated Cu K$\bar{\alpha}$ radiation (1.541 78 Å). A total of 3200 unique reflections were collected and, after correction for Lorentz, polarization, and background effects, 2057 (64%) were judged observed.[6] A phasing model was found routinely using direct methods, and hydrogen atoms were located in difference electron density syntheses following partial refinement. Block-diagonal least-squares refinements with anisotropic non-hydrogen atoms and isotropic hydrogens have converged to a standard crystallographic residual of

(1) Cimino et al. have isolated a highly oxygenated steroid from *Eudendrium sp.*, see: Cimino, G.; De Rosa, S.; De Stephano, S.; Sodano, G. *Tetrahedron Lett.* **1980**, *21*, 3303. We are not aware of any other natural products reported from hydroids.

(2) In a disk bioassay, garveatin A shows in vitro activity against *Staphylococcus aureus* (MIC; 2 μg/disk), *Bacillus subtilis* (MIC; 2 μg/disk), *Pythium ultimum* (MIC; 20 μg/disk), and *Rhizoctonia solani* (MIC; 20 μg/disk).

(3) Our tentative ^{13}C NMR assignments are 189.3 (C1), 106.7 (C2 or C8a), 181.5 (C3), 40.8 (C4), 119.6 (C5 or C10), 138.4 (C6 or C10a), 138.0 (C6 or C10a), 127.3 (C7), 155.8 (C8), 106.2 (C8a or C2), 106.7 (C8a or C2), 161.5 (C9), 110.9 (C9a), 114.1 (C10 or C5), 146.3 (C4a), 7.1 (C11), 28.9 (C12 and C13), 19.8 (C14), 204.7 (C15), 32.0 (C16).

(4) Triacetate 2 shows MS, M^+ m/z 466, 424, 382, 340 (base peak), 325; ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H), 1.80 (s, 3 H), 2.35 (s, 3 H), 2.38 (s, 3 H), 2.43 (bs, 3 H), 2.54 (s, 3 H), 2.55 (s, 3 H), 7.59 (bs, 1 H), 7.84 (s, 1 H). Triacetate 4 shows MS, M^+ m/z 466; ^1H NMR ($CDCl_3$) δ 1.53 (s, 6 H), 1.90 (s, 3 H), 2.05 (s, 3 H), 2.33 (s, 3 H), 2.38 (s, 3 H), 2.55 (bs, 3 H), 5.00 (d, J = 2 Hz, 1 H), 5.38 (d, J = 2 Hz, 1 H), 7.24 (s, 1 H), 7.45 (bs, 1 H), 15.33 (s, 1 H).

(5) Monache, F. D.; McQuhae, M. M.; Ferrari, F.; Marini-Bettolo, G. B. *Tetrahedron* **1979**, *35*, 2143.

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