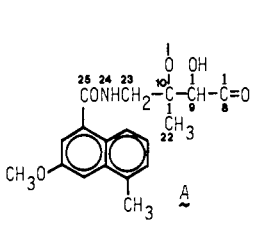
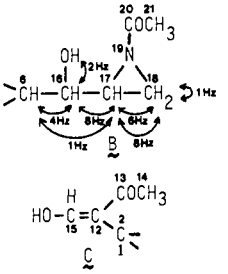
given above. The ^1H NMR spectrum was assigned by comparison with proton chemical shifts of related compounds as well as by spin-decoupling experiments. Carbon assignments were made by gated-decoupling and selective-proton-decoupling experiments. These data indicated that **1** consists of the following three structural units: A, B, and C.

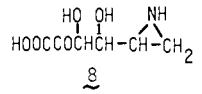


A

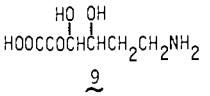


B

C



8



9

Unit A. Upon ammonolysis of **1**, (2*S*,3*S*)-2,3-dihydroxy-4-(3-methoxy-5-methylnaphthalene-1-carboxamido)-3-methylbutanamide (**5**) was formed from unit A.[1] The long-range coupling (J_{CH} = 4 Hz) observed between 9-OH (δ_H 8.20) and C-8 (δ_C 164.3) suggested an α-hydroxy carbonyl function.

Unit B. Spin-decoupling experiments on **1** showed the presence of a 1,1,3,4-tetrasubstituted-2-butanol structure. The long-range decouplings of 17-H (δ_H 3.39; δ_C 46.6 for C-17), 18-H_2 (δ_H 2.77 and 2.46; δ_C 36.7 for C-18) and 21-H_3 (δ_H 2.18; δ_C 20.8 for C-21) sharpened the signal of C-20 (δ_C 173.0), suggesting an acetylaziridine group at the 17- and 18-positions. Upon hydrogenation of **1** to **3**, the methylene group (C-18) was converted into a methyl group (δ_H 1.24, d, J_{HH} = 5 Hz, and δ_C 14.1, q), and the resonance of C-17 shifted downfield by 11.5 ppm. These observations were consistent with ring opening of the aziridine ring to the amide.

Unit C. Two carbons (C-14 and -15) bearing protons were confirmed by one-bond proton-decoupling experiments. Long-range proton-decoupling experiments on **1** showed that 15-OH (δ_H 12.16) is coupled to both C-15 (δ_C 151.0) (J_{CH} = 3 Hz) and C-12 (δ_C 118.7) (sharpened). Couplings between 15-H (δ_H ca. 7.35) and C-2 (δ_C 165.9) (J_{CH} = 6 Hz) and between 15-H and C-12 (sharpened) were observed. In addition, coupling between 14-H_3 (δ_H 2.29) and C-12 (sharpened) was observed. It was confirmed by long-range decoupling of 14-H_3 (J_{CH} = 4 Hz) that C-13 (δ_C 191.7) and C-14 (δ_C 24.3) constitute an acetyl group. Conversion of **1** and **3** into **2** and **4** shifted the resonances of 15-H downfield by ca. 1 ppm, respectively. Transformation of **3** to **4** shifted the resonance of C-15 upfield by 11.7 ppm.

Decoupling of 6-H (δ_H 5.50) sharpened the signals of C-4 (δ_C 162.1) and C-5 (δ_C 119.3). In addition, couplings between 6-H and C-2 (J_{CH} = 4 Hz) and between 16-H (δ_H 4.64) and C-5 (sharpened) were observed in **1**.

The most reasonable combination of these structural units (A, B, and C) with the remaining nitrogen (one) and oxygen (three) atoms leads to the 5,6-dihydro-4*H*-1,3-oxazine as a partial structure for **1**, to which the 1,3-dioxane ring is combined in a spiro form.

As reported previously,[1] hydrolysis of **1** with 5% aqueous ammonia followed by 20% hydrochloric acid afforded two acids (**6** and **7**), which arose from partial structure A, glycine, and an unidentified compound. The latter compound has been identified as pyridine hydrochloride by direct comparison with an authentic sample. Hydrolysis of the 7–8 bond and retro-aldol cleavage of the 9–10 bond would give glycolic acid, which reacts with ammonia to yield glycine.[9] Since the formation of pyridine was also observed in the hydrolysis of **1** with 20% hydrochloric acid, the nitrogen atom in the pyridine should not arise from ammonia. Hydrolysis of the 1–2, 3–4, 5–11, and 7–8 bonds would afford 3,4-dihydroxy-5,6-imino-2-oxohexanoic acid (**8**). On the other hand, formic acid would be formed by retro-Claisen cleavage of **C**. Reduction of **8** with the formic acid to form the primary amine (**9**), ring closure, twice dehydration and final decarboxylation would account for the formation of pyridine.

(9) The formation of glycine from glycolic acid under the same conditions as those employed for hydrolysis of **1** was confirmed.

Acknowledgment. We are indebted to Kyowa Hakko Kogyo Co., Ltd., for the supply of carzinophilin.

Registry No. 1b, 1403-29-8.

Supplementary Material Available: Tables of proton and carbon NMR spectra for **1**, **2**, **3**, and **4** (4 pages). Ordering information is given on any current masthead page.

Carbon–Carbon Bond Formation by Selective Coupling of Enol Silyl Ethers with Oxime Sulfonates

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We wish to outline a new reaction that leads to the formation of enaminones by the combination of enol silyl ethers and oxime sulfonates in the presence of organoaluminum reagents (Scheme I).[1,2] Enaminones (N—C=C—C=O) are an important class of compounds in view of the fruitful chemical properties and high synthetic utility, particularly as building blocks for the elaboration of fused carbocycles and polyheterocycles.[3,4] The general synthetic method involves reaction between β-diketones and amines that usually causes the lack of regiochemical control over the position of amino group in the enaminone moiety.[4]

A typical experimental procedure of the reaction is illustrated by the preparation of enaminone **3**. Diethylaluminum chloride (3 mmol, 3 mL of a 1 M hexane solution) was added to a mixture of *anti*-2-methylcyclohexanone oxime mesylate (**1**) (205 mg, 1 mmol)[5] and 2-(trimethylsiloxy)-1-octene (**2**) (220 mg, 1.1 mmol)[6] in dry methylene chloride at −78 °C. After 30 min, the solution was allowed to warm to 20 °C and stirred there for 1 h. The reaction was terminated by adding 10% NaOH. The crude

(1) For other classical reactions via nitrilium ions as intermediates, see reviews of the Ritter reaction: Johnson, F.; Madronero, R. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1966; Vol. 6, p 95. Krimen, L. I.; Cota, D. J. *Org. React. (N.Y.)* **1969**, *17*, 213. Meyers, A. I.; Sircar, J. C. In "The Chemistry of Cyano Group"; Rappoport, Z., Ed.; Interscience: New York, 1970; p 341.

(2) For relevant reactions by organoaluminum reagents, see: Hattori, K.; Matsumura, Y.; Miyazaki, T.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 7368. Sakane, S.; Matsumura, Y.; Yamamura, Y.; Ishida, Y.; Maruoka, K.; Yamamoto, H. *Ibid.* **1983**, *105*, 672.

(3) The term enaminone was used to indicate any compound containing the conjugated system N—C=C—C=O. For the designation, see the reviews in ref 4.

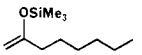
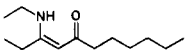
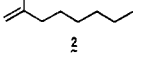
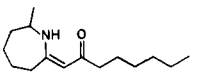
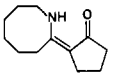
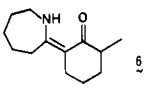
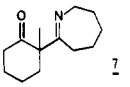
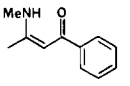
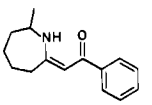
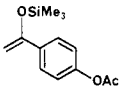
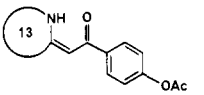
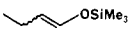
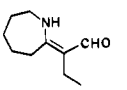
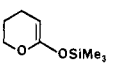
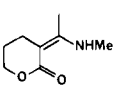
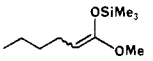
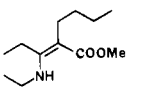
(4) For reviews, see: Nishino, T.; Kajima, C.; Omote, Y. *J. Synth. Org. Chem., Jpn.* **1976**, *34*, 526. Greenhill, J. V. *Chem. Soc. Rev.* **1977**, *16*, 277. See also: Natale, N. R. *Tetrahedron Lett.* **1982**, *23*, 5009. For recent synthetic applications of enaminones, see: Horii, Z.; Morikawa, K.; Ninomiya, I. *Chem. Pharm. Bull.* **1969**, *17*, 2230. Oishi, T.; Nagai, M.; Onuma, T.; Moriyama, H.; Tsutae, K.; Ochiai, M.; Ban, Y. *Ibid.* **1969**, *17*, 2306. Yamada, Y.; Matsui, M. *Agric. Biol. Chem.* **1971**, *35*, 282. Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Am. Chem. Soc.* **1978**, *100*, 3598. Patrick, J. B.; Saunders, E. K. *Tetrahedron Lett.* **1979**, 4009. Célérier, J.-P.; Eskénazi, C.; Lhommet, G.; Maitte, P. *J. Heterocycl. Chem.* **1979**, *16*, 953. Nagasaka, T.; Inoue, H.; Ichimura, M.; Hamaguchi, F. *Synthesis* **1982**, 848.

(5) Noncrystalline oxime mesylates may be conveniently stored at −20 °C or as a CH_2Cl_2 solution at 0 °C.

(6) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

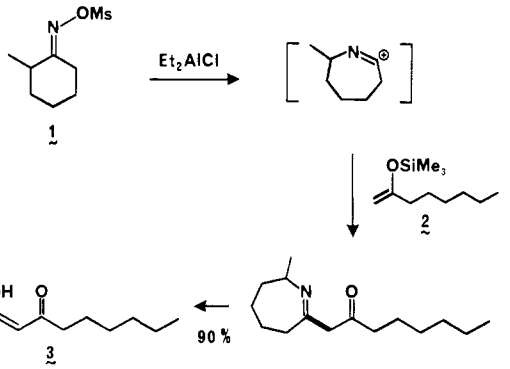
0002-7863/83/1505-6312$01.50/0

Table I. Condensation of Enol Silyl Ethers with Oxime Mesylates by Organoaluminum Reagents[a]

entry	enol silyl ether	oxime mesylate[b] R^1	oxime mesylate[b] R^2	method[c]	product[d]	yield,[e] %
1		Et	Et	A		95
2	 2			B	8	67
3		$-CHCH_3(CH_2)_4-$[f]		A		90
4				B	3	86
5		$-(CH_2)_6-$		A[g]		74
6		Me	Me	A		30
7				B		69
8	 4	$-(CH_2)_5-$		B	 6	82
9	 5	$-(CH_2)_5-$		B[g]	 7	42
10		Me	Me	A		65
11				B		31
12		$-CHCH_3(CH_2)_4-$[f]		A		66
13		$-(CH_2)_{11}-$		A		80
14		$-(CH_2)_5-$		B[g]		53
15		Me	Me	A		48
16		Et	Et	B		73

[a] Reaction performed on a 1-2 mmol scale. [b] Oxime mesylates of type R^1R^2C=NOMs were employed. [c] Method A: See the experimental procedure in text. Method B: Treatment with $EtAlCl_2$ (2 equiv, a 2 M toluene solution) at −78 °C for 30 min and at 20 °C for 0.5–1 h. [d] All products were identified by ^1H NMR and IR spectra. All new compounds gave satisfactory elemental analyses. [e] Isolated yield. [f] The anti isomer 1 was used. [g] The reaction was carried out at −78 °C for 1–3 h.

Scheme I



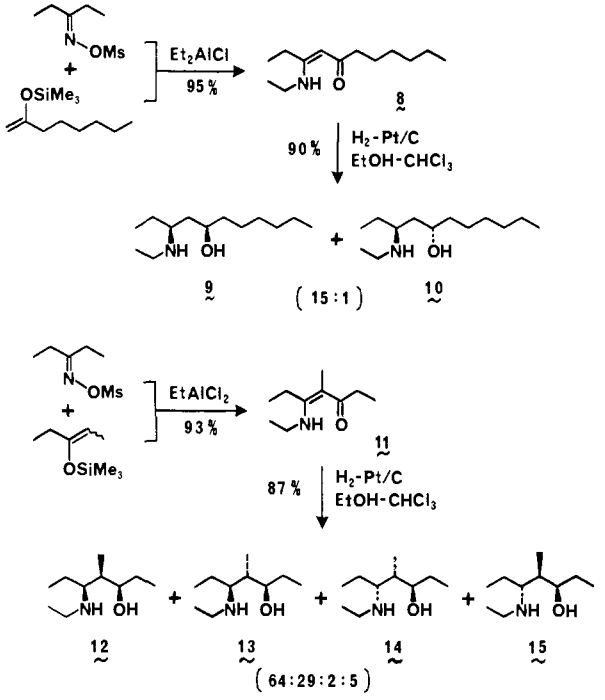
product was extracted with methylene chloride. The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residual material was subjected to column chromatography on silica gel (ether–hexane, 1:2 as eluant) to give the enaminone **3** (213 mg, 90% yield) as a colorless liquid.[7]

Some examples of the reaction are summarized in Table I. This method is applicable to a variety of enol silyl ethers and ketoxime sulfonates. Of all the Lewis acids examined diethylaluminum chloride and ethylaluminum dichloride (2–3 equiv) have proven to be the most efficacious, and other Lewis acids ($AlCl_3$, $SnCl_4$, $FeCl_3$, $TiCl_4$, Me_3SiOTf, Me_3SiI, etc.) gave less satisfactory results (0–35% yield). Notably, this condensation takes place regiospecifically in both substrates. For example, reaction of 1-(trimethylsiloxy)-6-methylcyclohexene (**4**) or 1-(trimethylsiloxy)-2-methylcyclohexene (**5**) with cyclohexanone oxime mesylate furnished **6** or **7**, respectively, as a sole isolable product (entries 8 and 9). The regiospecific Beckmann rearrangement was observed in the case of the unsymmetrical oxime sulfonates (entries 3, 4, and 12). Another striking feature of the reaction is the high chemospecificity. Thus, the condensation of the enol silyl ether derived from *p*-acetoxyacetophenone occurred specifically with

(7) ^1H NMR (CCl_4) δ 10.74 (1 H, br s, NH), 4.74 (1 H, s, NC=CH), 3.52 (1 H, m, NCH); IR (CCl_4) 3450, 1604, 1578 cm^{-1}.

oxime mesylates, and the acetoxy moiety was left intact (entry 13). It should be added that oxime sulfonates of aromatic ketone and cyclopentanone systems are not employable; attempted condensation of various oxime substrates resulted in the formation of deteriorated reaction mixtures.

The versatility of enaminones in synthetic as well as heterocyclic chemistry serves as a stimulus for exploration of the potential applications of this methodology.[4] Accordingly, we have devised a new stereoselective approach to γ-amino alcohols by a direct hydrogenation of the enaminones.[8] Thus, the selective hydrogenation of the enaminone **8** leading to the γ-amino alcohol **9** was realized in 90% yield with reasonable stereoselectivity (~94%)[9] by using 10% platinum on charcoal as a catalyst in EtOH–$CHCl_3$ (30:1)[10] at 20 °C for 6 h and 1 atm of H_2. Under the similar conditions, the enaminone **11** was converted to the γ-amino alcohols, **12–15** (87% yield) in a ratio of 64:29:2:5.[11] Again 1,3-



stereochemical control in **11** reaches to ~13:1 (64 + 29:2 + 5), which takes precedence over the 1,2 effect. These two examples clearly indicated the rigorous 1,3-stereochemical regulations exercised by an neighboring amino group in acyclic systems to the extent of 13–15:1. Such intramolecular participation of an appropriately placed heteroatom promises to be a useful strategy in the stereocontrolled synthesis of acyclic systems, since it is an effective way to reduce the conformational mobility and to increase the free energy difference of diastereomeric transition states.[12]

Acknowledgment. This work was supported by the Ministry of Education, Japanese Government (Grant-in-aid 118006).

Registry No. 2, 55314-45-9; **3**, 86921-54-2; **4**, 19980-33-7; **5**, 19980-35-9; **6**, 86921-55-3; **7**, 86921-56-4; **8**, 86921-57-5; **9**, 86921-58-6; **10**, 86953-18-6; **11**, 86921-59-7; **12**, 86921-60-0; **13**, 86992-31-6; **14**, 86992-32-7; **15**, 86992-33-8; (*E*)-$CHCH_3(CH_2)_4$—C=NOMs, 86921-61-1; $-(CH_2)_6$—C=NOMs, 80053-71-0; Me_2C=NOMs, 86921-62-2; $-(CH_2)_3$—C=NOMs, 80053-69-6; $-(CH_2)_{11}$—C=NOMs, 80053-72-1; Et_2C=NOMs, 86921-63-3; $EtAlCl_2$, 563-43-9; Et_2AlCl, 96-10-6; (1-cyclopenten-1-yloxy)trimethylsilane, 19980-43-9; (1-cyclohexen-1-yloxy)trimethylsilane, 6651-36-1; trimethyl[(1-phenylethenyl)oxy]silane, 13735-81-4; [[α-(4-acetoxyphenyl)ethenyl]oxy]silane, 86941-88-0; (1-butenyloxy)trimethylsilane, 6651-33-8; [(3,4-dihydro-2*H*-pyran-6-yl)oxy]trimethylsilane, 71309-70-1; [[(α-methoxy)hex-1-enyl]oxy]trimethylsilane, 84393-11-3; 2-(cyclopentan-1-on-2-ylidene)octahydrazocine, 86921-64-4; 2-[(α-methylamino)ethanylidene]cyclohexanone, 86921-65-5; 3-(methylamino)-1-phenyl-2-buten-1-one, 14091-93-1; 2-[(phenylcarbonyl)methylene]-7-methylhexahydro-1*H*-azepine, 86921-66-6; 2-[[(4-acetoxyphenyl)carbonyl]methylene]azacyclotridecane, 86921-67-7; 2-[(α-formyl)propylidene]hexahydro-1*H*-azepine, 86921-68-8; 3-[(α-methylamino)ethylidene]-2*H*-pyran-2-one, 86921-69-9; methyl 2-butyl-3-ethylaminopent-2-enoate, 86921-70-2.

(8) For recent stereoselective synthesis of γ-amino alcohols, see: Kozikowski, A. P.; Chen, Y. Y. *J. Org. Chem.* **1981**, *46*, 5248. Wang, Y.-F.; Izawa, T.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1982**, *104*, 6465. Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *Tetrahedron Lett.* **1982**, *23*, 619. Müller, I.; Jäger, V. *Ibid.* **1982**, *23*, 4777.

(9) The ratio of **9**/**10** was determined by GLC assay (OV-101, 205 °C) as their acetyl derivatives, **16** and **17**: t_r(**16**) = 8.30 min; t_r(**17**) = 9.21 min. The authentic **16** and **17** were prepared from 1-octene by the following sequence: (a) 2-isoxazoline formation (*n*-$PrNO_2$, PhNCO, cat. NEt_3); (b) reduction ($LiAlH_4$), followed by acetylation (Ac_2O, Py); (c) separation of two diastereomers by column chromatography on silica gel; (d) reduction of each isomer ($LiAlH_4$), followed by acetylation (Ac_2O, Py) leading to **16** and **17**, respectively. The stereochemical assignments of **16** and **17** were made according to the following literature: Jäger, V.; Buss, V.; Schwarb, W. *Tetrahedron Lett.* **1978**, 3133.

(10) Secrist, J. A.; III; Louge, M. W. *J. Org. Chem.* **1972**, *37*, 335. Palladium on charcoal is not effective for the reduction of **8** under comparable reaction conditions.

(11) Determined by GLC assay (OV-101, 190 °C) after conversion to the corresponding acetyl derivatives, **18–21**: t_r(**18**) = 5.26 min; t_r(**19**) = 5.60 min; t_r(**20**) = 6.19 min; t_r(**21**) = 6.96 min. The authentic specimen, **18** and **21**, were made from *cis*-2-pentene in an analogous fashion as described in ref 9. For preparation of the authentic **20**, the acetyl derivative **18** was transformed into a mixture of **18** and **20** by the sequence: (a) selective hydrolysis of the acetoxy moiety (K_2CO_3, MeOH); (b) oxidation of the alcohol ($(COCl)_2$, Me_2SO, NEt_3); (c) reduction of the ketone ($NaBH_4$); (d) acetylation of the resulting two isomers (Ac_2O, Py).

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A Novel (η^5-Cyclohexadienyl)tricarbonylchromium Anion: The Reaction between the Dianion of (η^6-Naphthalene)tricarbonylchromium and a Proton Source

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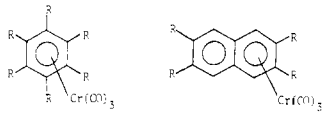
Nonaqueous electrochemical studies on the reductive behavior of various types of (arene)tricarbonylchromium complexes have been reported.[1-8] Of interest is the fact that exhaustive reduction of (benzene)tricarbonylchromium complexes (I) or (naphtha-



lene)tricarbonylchromium complexes (II) in the presence of a proton source generates a solution with an oxidative wave at approximately −0.5 V. Oxidation at −0.4 V regenerates the original complexes.[1,7]

This behavior prompted us to investigate the product of the reaction between the dianion of (naphthalene)tricarbonylchromium and a proton source. We now wish to report our preliminary findings. Reaction of 50 mL of a 20 mM solution of (η^6-

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