An Effective and Selective Conjugate Propargylation Reaction of Stannylallenes to α,β-Unsaturated Carbonyl Compounds and α-Nitro Olefins

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Stannylallenes (1) reacted with α,β-unsaturated carbonyl compounds and α-nitro olefins in the presence of $TiCl_4$ to give the corresponding conjugate propargylation products. Thus, the reaction of 1 with cyclic and acyclic α,β-unsaturated carbonyl compounds (2) gave β-propargylic ketones (3) in high yields. With α-nitro olefins (4), two types of products, β-propargylic nitroalkanes (5) and α-propargylic ketones (6), were obtained selectively depending on the presence or absence of the α-substituent of 4. Transformations of the products (6) to cyclopentenone derivatives (10 and 12) are also described.

The synthetic utility of the carbon–carbon triple bond is well recognized in versatile transformations to other functional groups, ring construction represented by 1,3-dipolar cycloadditions and Diels–Alder reactions, carbon chain elongation, and so on.[1] Metal acetylides are generally used for the introduction of the triple bond, while growing attention has recently been drawn toward direct propargylation using propargylic or allenic metal reagents.[1,2] However, this method often suffers from the difficulties in controlling the ambident behavior of the reagents, because propargylic and allenic metal compounds are often in equilibrium and the reaction of these reagents with electrophiles affords a mixture of propargylic and allenic adducts.[1-3] Selective propargylation methods have been extensively studied, changing the metal as well as the reaction conditions.[4-10] Most of the reagents developed are unstable, and so used after preparation in situ, while silylallenes,[11] allenic organomercurials,[12] and stannylallenes[13] are isolable and were reported to work as propargylic anion equivalents.

We have been interested in the readily available and easy-handling stannylallenes. Their potency of selective propargylation reaction was shown in the reaction with heteroatom electrophiles and a reactive aldehyde nearly two decades ago.[13] Very recently, carbon–carbon bond forming reactions of stannylallenes with allyl acetates,[14] acetals,[15] quinolines,[16] or 4-acetoxy-2-azetidinone[17] were reported. In this paper we describe the regioselective conjugate propargylation of stannylallenes to α,β-unsaturated carbonyl compounds and α-nitro olefins coupled with some transformations of the products.

Results and Discussion

Reaction of Stannylallenes with α,β-Unsaturated Carbonyl Compounds. Conjugate addition of allylic metal reagents to α,β-unsaturated carbonyl compounds is well established and has been widely used as a synthetic method for carbon–carbon bond formation.[18] In contrast to the extensive studies on conjugate allylation, conjugate propargylation of α,β-unsaturated carbonyl compounds with propargylic or allenic metal reagents has been limited to a few examples in spite of the synthetic utility of the propargylic moiety. These facts may arise from the difficulties in controlling the addition mode (1,2- vs 1,4-addition) as well as the ambident behavior of the reagents. Corey et al. reported a single example of regioselective conjugate propargylation using lithio-1-(triisopropylsilyl)propyne to 2-cyclohexenone in high yield.[4b] Utiliza-

(1) A review: *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978.

(2) Reviews: (a) Moreau, J.-L. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Part 1, pp 363–413. (b) Epsztein, R. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B, pp 107–176. (c) *Allenes in Organic Synthesis*; Schuster, H. F., Coppola, G. M., Eds.; Wiley: New York, 1984.

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(4) Lithium reagents: (a) Yamakado, Y.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 5568. (b) Corey, E. J.; Rucker, C. *Tetrahedron Lett.* **1982**, *23*, 719. (c) Michelot, D. *Synth. Commun.* **1989**, *19*, 1705. See also ref 3.

(5) Magnesium reagents: (a) Roumestant, M. L.; Place, P.; Gore, J. *Tetrahedron* **1977**, *33*, 1283. (b) Moreau, J.-L.; Frangin, Y.; Gaudemar, M. *Bull. Soc. Chim. Fr.* **1970**, 4511. (c) Wender, P. A.; Harmata, M.; Jeffrey, D.; Mukai, C.; Suffert, J. *Tetrahedron Lett.* **1988**, *29*, 909. See also ref 4a.

(6) Titanium reagents: (a) Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Org. Chem.* **1982**, *47*, 2225. (b) Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768.

(7) Aluminum reagents: Hahn, G.; Zweifel, G. *Synthesis* **1983**, 883.

(8) Boron reagents: (a) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1978**, *100*, 5561. (b) Haruta, R.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *Ibid.* **1982**, *104*, 7667. (c) Ikeda, N.; Arai, I.; Yamamoto, H. *Ibid.* **1986**, *108*, 483.

(9) Copper reagents: (a) Ganem, B. *Tetrahedron Lett.* **1974**, 4467. (b) Paquette, L. A.; Han, Y.-K. *J. Am. Chem. Soc.* **1981**, *103*, 1831.

(10) Zinc reagents: (a) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774. (b) Zweifel, G.; Hahn, G. *J. Org. Chem.* **1984**, *49*, 4565.

(11) (a) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925. (b) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *Ibid.* **1986**, *51*, 3870.

(12) Larock, R. C.; Chow, M.-S.; Smith, S. J. *J. Org. Chem.* **1986**, *51*, 2623.

(13) (a) Kuivila, H. G.; Cochran, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 7152. (b) Kitching, W.; Fong, C. W.; Smith, A. J. *Ibid.* **1969**, *91*, 767. (c) Bullpitt, M. L.; Kitching, W. *J. Organomet. Chem.* **1972**, *34*, 321. (d) Sipeuhou Simo, M.; Jean, A.; Lequan, M. *Ibid.* **1972**, *35*, C23. (e) Lequan, M.; Guillerm, G. *Ibid.* **1973**, *54*, 153.

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(17) Selective propargylation of 4-acetoxy-2-azetidinone with 3-methyl-1-(tri-*n*-butylstannyl)allene was applied to a novel 1β-methylcarbapenem synthesis: Haruta, J.; Nishi, K.; Kikuchi, K.; Matsuda, S.; Tamura, Y.; Kita, Y. *Chem. Pharm. Bull.* **1989**, *37*, 2338.

(18) Reviews: (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 173–205. (b) Hosomi, A.; Sakurai, H. *Yuki Gosei Kagaku Kyokai Shi* **1985**, *43*, 406. (c) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745. (d) Majetich, G.; Defauw, J. *Tetrahedron* **1988**, *44*, 3833. (e) Schinzer, D.; Allagiannis, C.; Wichmann, S. *Ibid.* **1988**, *44*, 3851.

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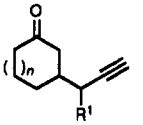
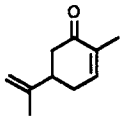
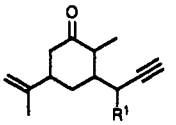
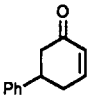
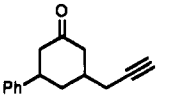
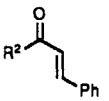
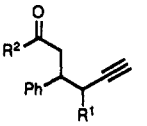
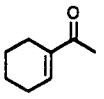
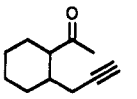
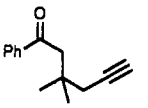
Table I. Propargylation of α,β-Unsaturated Carbonyl Compounds (2) Using Stannylallenes (1a,b)

entry	α,β-enone 2	stannylallene 1	reaction conditions	product 3	yield,[a] %
1	 **2a**: n = 1	**1a**	−40 °C, 0.5 h	 **3a**: n = 1; R^1 = H	78
2	**2a**	**1b**	−40 °C, 0.5 h	**3b**: n = 1; R^1 = Me[b]	86
3	**2b**: n = 0	**1a**	−40 °C, 1.5 h	**3c**: n = 0; R^1 = H	59
4	**2c**: n = 2	**1a**	−78 °C, 1 h	**3d**: n = 2; R^1 = H	60
5	 **2d**	**1a**	−40 → 0 °C, 1 h	 **3e**: R^1 = H[b]	86
6	**2d**	**1b**	−40 °C, 1.5 h	**3f**: R^1 = Me[b]	81
7	 **2e**	**1a**	−40 °C, 0.75 h	 **3g**[b]	67
8	 **2f**: R^2 = Ph	**1a**	−40 → 0 °C, 1 h	 **3h**: R^1 = H; R^2 = Ph	86
9	**2f**	**1b**	−40 °C, 0.5 h	**3i**: R^1 = Me; R^2 = Ph[b]	88
10	**2g**: R^2 = Me	**1a**	−40 → 0 °C, 1.5 h	**3j**: R^1 = H; R^2 = Me	68
11	 **2h**	**1a**	−40 → 0 °C, 8.5 h	 **3k**[b]	54
12	 **2i**	**1a**	−40 °C, 7 h	 **3l**	59

[a] Isolated yields based on **2**. [b] A mixture of diastereomers. The ratios determined by ^{1}H NMR analyses are as follows: **3b**, 1:1.1; **3e**, 1:1:2.5:2.5; **3f,g**, not determined; **3i**, 1:1.2; **3k**, 1:6.

tion of organocopper reagents[19] or silylallenes[20] for 1,4-addition to α,β-unsaturated carbonyl compounds gave unsatisfactory yields of the products. For instance, the reaction of silylallene ($H_2C{=}C{=}CHSiMe_3$) with 2-cyclohexenone in the presence of $TiCl_4$ provided a 1.6:1 mixture of the 1,4-adduct, 3-propargylcyclohexanone, and a cyclopentene derivative.[20] In connection with this study, we have recently communicated[21] that the reaction of stannylallene (**1**) with α,β-unsaturated carbonyl compounds (**2**) including 2-cyclohexenone (**2a**) in the presence of $TiCl_4$ proceeded regioselectively to give the conjugate propargylation products (**3**). We now give here a full account of the work.

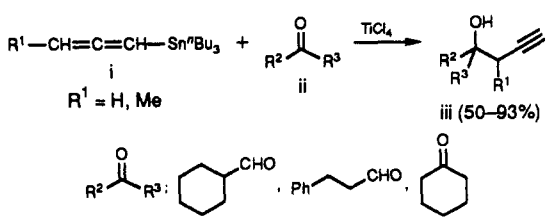
A typical procedure for the formation of the propargylation product (**3a**) by reaction of **2a** with (triphenylstannyl)allene (**1a**) is as follows: Treatment of **2a** with **1a** in the presence of 1.2 equiv of $TiCl_4$ in methylene chloride at −40 °C for 0.5 h gave **3a** in 78% yield after chromatographic purification. None of the 1,2-adduct and allenic products were detected by thin-layer chromatography (TLC) and IR and 500-MHz ^{1}H NMR spectra of the crude product. Other Lewis acids such as $SnCl_4$, $AlCl_3$, $EtAlCl_2$, $ZrCl_4$, $BF_3{\cdot}OEt_2$, Me_3SiCl, and $Me_3SiOSO_2CF_3$ caused no reaction or gave a complex mixture,[22] and the best results were obtained by the use of $TiCl_4$. The use of ZnI_2 resulted in reversal of the regioselectivity, producing the 1,2-adduct, 1-propargyl-2-cyclohexenol as a sole product in 72% yield.[25] The reason for this change in regioselectivity is

(19) Reaction of a complex of propargylmagnesium reagent and CuBr with an α,β-enone gave β-propargylic ketone in 40% yield.[9b]

(20) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (b) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935.

(21) Haruta, J.; Nishi, K.; Matsuda, S.; Tamura, Y.; Kita, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1065.

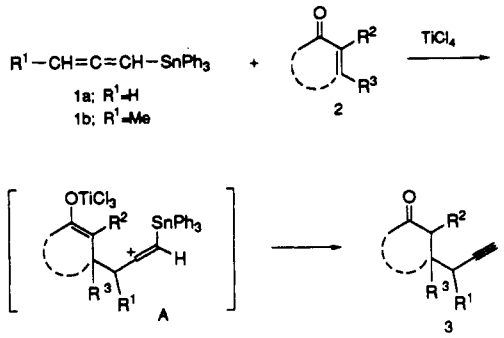
(22) Reaction of (tri-*n*-butylstannyl)allene with aldehydes in the presence of dibutyldichlorotin gave a mixture of propargylic and allenic alcohols.[23] On the other hand, we found that (tri-*n*-butylstannyl)allenes (i) reacted with carbonyl compounds (ii) in the presence of 1.2 equiv of $TiCl_4$ in CH_2Cl_2 at −78 °C to give β-propargylic alcohols (iii) in high yields. None of the allenic adducts were detected in the crude products.[24]



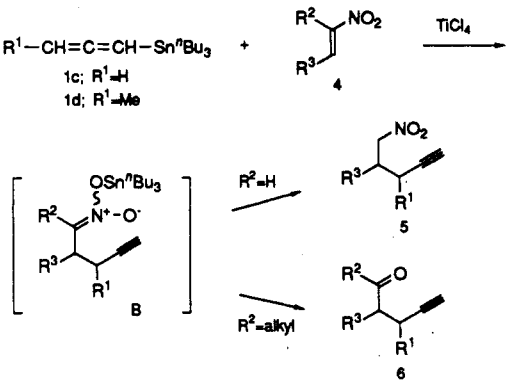
(23) Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1985**, *297*, 149.

(24) These results were presented at the Japanese–United States Congress of Pharmaceutical Sciences, Honolulu, HI, December 1987, Poster Abstracts, p S226.

Scheme I



Scheme II



not yet clear. Similarly 3-methyl-1-(triphenylstannyl)-allene (**1b**) reacted with **2a** to give the 1,4-adduct (**3b**) as a 1:1 mixture of two diastereomers. A series of other α,β-unsaturated carbonyl compounds (**2b–i**) was similarly treated with stannylallenes (**1a,b**) to give the corresponding β-propargylic carbonyl compounds (**3c–l**) in high yields. The results are summarized in Table I. The present method was found to be effective for the conjugate propargylation of both cyclic (**2a–e**) and acyclic α,β-unsaturated carbonyl compounds (**2f–i**).

It is presumed that the stannylallene (**1**) reacts with **2** at the γ-position to give initially a vinyl cation intermediate (A) stabilized through hyperconjugation with C–Sn σ-bond,[26] and removal of the stannyl group occurs readily to afford **3** selectively (Scheme I). These results are in contrast to the reaction of silylallenes and α,β-unsaturated carbonyl compounds reported by Danheiser et al.[20] The conjugate addition of silylallene to the enone gave vinyl cation like A, from which 1,2-migration of the silyl group occurred, followed by cyclization reaction to give 3-acyl-1-silylcyclopentene. These differences may be accounted for, in part, by the weaker C–Sn bond (about 60 kcal/mol) than the C–Si bond (about 80 kcal/mol).[27]

Conjugate Addition of Stannylallenes to α-Nitro Olefins. Since a nitro group can be converted to various functional groups, carbon–carbon bond formation by a conjugate addition of carbon nucleophiles to α-nitro olefins provides a powerful method for organic synthesis.[28] Especially in view of the facts that the nitro groups are synthetically equivalent to the carbonyl groups and α-nitro olefins provide an umpolung of reactivity of the carbonyl derivatives,[29] addition reactions of carbon nucleophiles such as lithium enolates,[30] silyl enol ethers,[29b,31] tin(II) enolates,[32] enamines,[33] allylsilanes,[34] allylstannanes,[35] organoaluminum reagents,[29c,36] or aromatic compounds[37] to α-nitro olefins have been successfully developed. We extended our $TiCl_4$-mediated conjugate addition of stannylallenes to the propargylation of α-nitro olefins.

Though the addition of (triphenylstannyl)allene (**1a**) to α-nitro olefins (**4**) under the usual conditions ($TiCl_4$, CH_2Cl_2, −40 °C to room temperature) proceeded slowly, active (tri-*n*-butylstannyl)allene (**1c**) smoothly reacted to give a high yield of the conjugate addition product. Thus, **1c** and **4a** were stirred in the presence of 1.2 equiv of $TiCl_4$ in methylene chloride at −78 °C to give β-propargylic nitroalkane (**5a**) as a single product in 82% yield. Similar product (**5b**) was also obtained from the 3-methyl derivative (**1d**) and **4a** as a 1:1 mixture of two diastereomers in 82% yield. On the other hand, **1c** added to α-methyl nitro olefin (**4c**) under similar conditions to give two products monitored by TLC. When a mixture of the crude products was treated with 3 N HCl in THF at room temperature, the more polar product was converted to the less polar one, which turned out to be a hydrolyzed adduct, α-propargylic ketone (**6a**) and was obtained in 50% yield. Reaction of **1c** and **1d** with a variety of α-nitro olefins (**4a–f**) was examined, and the results are summarized in Table II. As shown in the table, two types of products, β-propargylic nitroalkanes and α-propargylic ketones, were obtained in good yields selectively from α-unsubstituted nitro olefins and α-alkylated ones, respectively. Only one example similar to our results has been reported on the reaction of a silylallene with a α-nitro olefin by Danheiser et al.[20b] Thus, 1-methyl-1-(trimethylsilyl)allene reacted with α-nitro olefin (**4b**) in the presence of $TiCl_4$ to give the conjugate propargylation product, 5-(nitromethyl)-7-phenyl-2-heptyne in 58% yield.

The following mechanism is proposed for the present results.[38] Conjugate addition of **1** to **4** affords a nitronate intermediate (B). In the case of α-unsubstituted nitro olefins (entries 1–4), the nitronate form undergoes protodestannylation, thus giving **5** on aqueous workup. On the other hand, α-alkylated nitro olefins (entries 5–11) react with **1** to generate more stable intermediates (B), which are directly hydrolyzed to ketone (**6**) by Nef type reaction (Scheme II). Formation of B is supported by characteristic spectral data for the crude product before acidic

(25) This reaction did not proceed at −40 °C, but it was completed at room temperature for 8 h.

(26) Zhai, D.; Zhai, W.; Williams, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 2501. And references cited therein.

(27) It had been stated in the reaction of allylstannanes: (a) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Chem. Lett.* **1979**, 977. (b) Naruta, Y.; Nagai, N.; Arita, Y.; Maruyama, K. *Ibid.* **1983**, 1683. (c) Uno, H. *J. Org. Chem.* **1986**, *51*, 350.

(28) (a) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, *100*, 6294. (b) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia*, **1979**, *33*, 1. (c) Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751. (d) Ono, N.; Kaji, A. *Synthesis* **1986**, 693.

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(30) (a) Miyashita, M.; Yamaguchi, R.; Yoshikoshi, A. *J. Org. Chem.* **1984**, *49*, 2857. (b) Haner, R.; Laube, T.; Seebach, D. *Chimia*, **1984**, *38*, 255. (c) Miyashita, M.; Awen, B. Z. E.; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun.* **1989**, 841. See also: (d) Yanami, T.; Ballatore, A.; Miyashita, M.; Kato, M.; Yoshikoshi, A. *Synthesis* **1980**, 407. (e) Escribano, F. C.; Alcantara, M. P. D.; Gomez-Sanchez, A. *Tetrahedron Lett.* **1988**, *29*, 6001.

(31) Seebach, D.; Brook, M. A. *Helv. Chim. Acta* **1985**, *68*, 319.

(32) Stevens, R. W.; Mukaiyama, T. *Chem. Lett.* **1985**, 855.

(33) (a) Blarer, S. J.; Schweizer, W. B.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 1637. (b) Seebach, D.; Beck, A. K.; Golinski, J.; Hay, J. N.; Laube, T. *Ibid.* **1985**, *68*, 162.

(34) (a) Ochiai, M.; Arimoto, M.; Fujita, E. *Tetrahedron Lett.* **1981**, *22*, 1115. (b) Uno, H.; Fujiki, S.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1267.

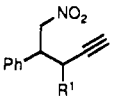
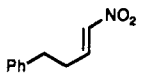
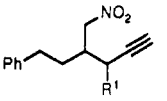
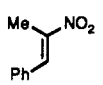
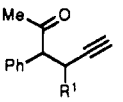
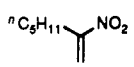
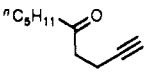
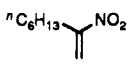
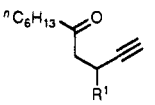
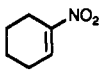
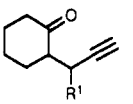
(35) Yamamoto, Y.; Nishii, S. *J. Org. Chem.* **1988**, *53*, 3597.

(36) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1989**, *54*, 2391.

(37) Lee, K.; Oh, D. Y. *Tetrahedron Lett.* **1988**, *29*, 2977.

(38) Yanami, T.; Kato, M.; Miyashita, M.; Yoshikoshi, A.; Itagaki, Y.; Matsuura, K. *J. Org. Chem.* **1977**, *42*, 2779.

Table II. Propargylation of α-Nitro Olefins (4) Using Stannylallenes (1c,d)

entry	α-nitro olefin 4	stannylallene 1	reaction procedure[a]	product 5, 6	yield,[b] %
1	 4a	1c	A	 5a: R^1 = H	82
2	4a	1d	A	5b: R^1 = Me[c]	82
3	 4b	1c	A	 5c: R^1 = H	76
4	4b	1d	A	5d: R^1 = Me[c]	71
5	 4c	1c	B	 6a: R^1 = H	50
6	4c	1d	B	6b: R^1 = Me[c]	61
7	 4d	1c	B	 6c	81
8	 4e	1c	B	 6d: R^1 = H	85
9	4e	1d	B	6e: R^1 = Me	73
10	 4f	1c	B	 6f: R^1 = H	73
11	4f	1d	B	6g: R^1 = Me[c]	71

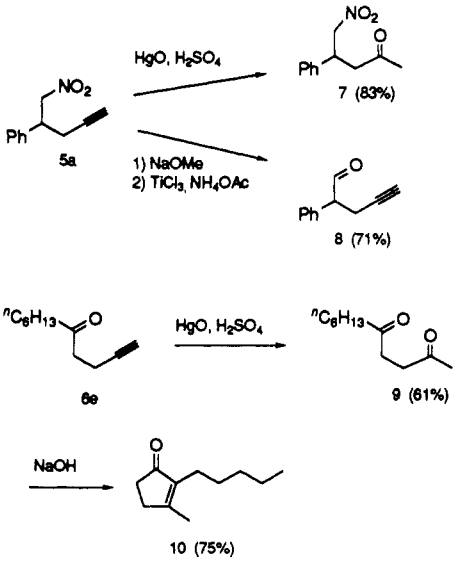
[a] A: $TiCl_4$ treatment. B: $TiCl_4$ treatment followed by 3 N HCl treatment. For detailed reaction conditions refer to the Experimental Section. [b] Isolated yields based on 4. [c] A mixture of diastereomers. The ratios determined by ^1H NMR analyses are as follows: **5b**, 1:1; **5d**, 1:2.4; **6b**, 1:1.6; **6g**, 1:3.

treatment in entry 5, absorption bands at 3310 and 2120 cm^{-1} (C≡CH) and 1605 cm^{-1} (C=N) in the IR spectra and a signal at δ 1.90 (s, CH_3C=N) in the ^1H NMR spectra. Similar behavior was also reported for Lewis acid mediated reactions of silyl enol ethers[29b] or allylsilanes[34b] with α-nitro olefins.

Some transformations of the functional groups were examined to demonstrate the synthetic utility of the products. Compounds **5** have the two carbonyl-equivalent groups, nitro and acetylenic groups, which were converted to the carbonyl groups independently. For instance, **5a** was treated with mercuric oxide and sulfuric acid in THF to give nitro ketone (**7**) in 83% yield, while **5a** was subjected to the Nef reaction (NaOMe then $TiCl_3$ and NH_4OAc)[39] to give propargylic aldehyde (**8**) in 71% yield. Synthesis of dihydrojasmone (**10**)[29a,c] was achieved from **6e** via 1,4-diketone (**9**) in two steps (Scheme III).

An efficient transformation of the terminal acetylenic bonds into α-hydroxy ketones developed in our laboratory[40] was applied to the α-propargylic ketones (**6**). Though the ordinary conditions [$PhI(OCOCF_3)_2$ (PIFA), $CHCl_3$–CH_3CN–H_2O, reflux] were not suitable for **6**, giving a complex mixture, probably due to resultant trifluoroacetic acid, a modified procedure using a basic buffer was effective: Without any protection of the carbonyl group, **6e** was treated with PIFA in the presence of K_2CO_3 at room

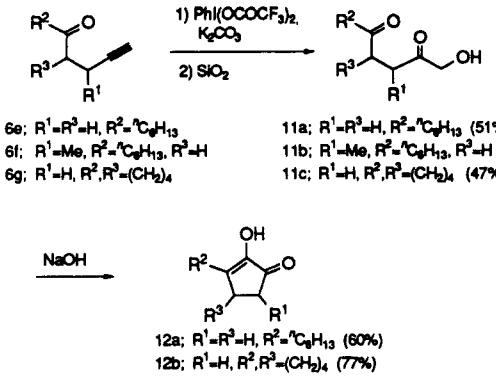
Scheme III



temperature to give hydroxy diketone (**11a**) in 55% yield after silica gel treatment. Similar direct conversions from **6f** and **6g** to **11b** and **11c**, respectively, were achieved. An application of these products was shown by their cyclization to 2-hydroxy-2-cyclopentenones. For instance, **11a** and **11c** were treated with NaOH in refluxing MeOH to give 2-hydroxy-2-cyclopentenones (**12a** and **12b**) in 60% and 77% yields, respectively (Scheme IV). This method

(39) McMurry, J. E.; Melton, J. *J. Org. Chem.* **1973**, *38*, 4367.
(40) (a) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *Tetrahedron Lett.* **1985**, *26*, 3837. (b) Kita, Y.; Yakura, T.; Terashi, H.; Haruta, J.; Tamura, Y. *Chem. Pharm. Bull.* **1989**, *37*, 891.

Scheme IV



6e; R^1=R^3=H, R^2=^{n}C$_6$H$_{13}$
6f; R^1=Me, R^2=^{n}C$_6$H$_{13}$, R^3=H
6g; R^1=H, R^2,R^3=(CH$_2$)$_4$

11a; R^1=R^3=H, R^2=^{n}C$_6$H$_{13}$ (51%)
11b; R^1=Me, R^2=^{n}C$_6$H$_{13}$, R^3=H (55%)
11c; R^1=H, R^2,R^3=(CH$_2$)$_4$ (47%)

12a; R^1=R^3=H, R^2=^{n}C$_6$H$_{13}$ (60%)
12b; R^1=H, R^2,R^3=(CH$_2$)$_4$ (77%)

provides a convergent strategy for synthesis of alkylated 2-hydroxy-2-cyclopentenones, which are of interest in flavor chemistry.[41]

In conclusion, an effective conjugate propargylation of α,β-unsaturated carbonyl compounds and α-nitro olefins by using stannylallenes was accomplished in the presence of $TiCl_4$. Studies on the extension of the present propargylation to other electrophiles are in progress.

Experimental Section

All boiling and melting points are uncorrected. IR and UV absorption spectra were recorded in $CHCl_3$ and EtOH, respectively. ^{1}H NMR spectra were measured at 90 or 500 MHz with $CDCl_3$ as a solvent. Mass spectra (MS) and high-resolution MS were obtained with a direct inlet system. Column chromatography was performed on E. Merck silica gel 60 (70–230 mesh ASTM) or E. Merck aluminum oxide 90 (70–230 mesh ASTM). For preparative TLC, E. Merck silica gel 60 GF_{254} was used. Organic layers were dried with anhydrous $MgSO_4$. Known compounds (**1c**,[23] **1d**,[17] **2e**,[42] **2i**,[43] and **4c**[44]) were prepared by the reported methods. α-Nitro olefins (**4d**[45] and **4e**[46]) were prepared by nitromercuration of the corresponding olefins and the subsequent elimination of mercury.[28a] Stannylallenes (**1a** and **1b**) and α-nitro olefin (**4b**) were prepared as follows. All other substrates are commercially available. The purity of all title compounds was judged to be more than 90–95% by ^{1}H NMR (mainly by 500-MHz NMR) determination.

(Triphenylstannyl)allene (1a). Under a nitrogen atmosphere, triphenylstannyl chloride (24.5 g, 0.062 mol) and NaI (9.3 g, 0.062 mol) were stirred in anhydrous THF (90 mL) at room temperature for 2.5 h. The resulting suspension was added to a solution of allenylmagnesium bromide in ether prepared from propargyl bromide (33.3 g, 0.28 mol) and magnesium turnings (4.5 g, 0.19 mol) according to the reported procedure[23] over 30 min. After being stirred overnight at room temperature, the reaction was quenched with saturated aqueous NH_4Cl (200 mL), and the organic layer was separated. The aqueous layer was extracted with ether (2 × 100 mL), and the combined organic layer was washed with brine, dried, and concentrated in vacuo. The residue was purified by column chromatography on aluminum oxide containing 5% water (*n*-hexane) to give a 50% yield (12.3 g) of **1a** as colorless crystals: mp 58.5–60 °C (MeOH) (lit.[47] mp 52–54 °C); IR 1925 cm^{-1}; ^{1}H NMR δ 4.35 (d, 2 H, J = 7 Hz), 5.37 (t, 1 H, J = 7 Hz), 7.2–7.6 (m, 15 H).

1-(Triphenylstannyl)-1,2-butadiene (1b) was prepared from 1-bromo-1,2-butadiene by the successive treatment with *n*-BuLi and triphenylstannyl chloride similarly as described for the preparation of **1d**.[17] A colorless gum (lit.[47] mp 35–36 °C): IR 1930 cm^{-1}; ^{1}H NMR δ 1.57 (dd, 3 H, J = 7, 4 Hz), 4.71 (quintet, 1 H, J = 7 Hz), 5.35 (dq, 1 H, J = 7, 4 Hz), 7.25–7.6 (m, 15 H).

1-Nitro-4-phenyl-1-butene (4b) was prepared from 3-phenylpropanal and nitromethane by fluoride-catalyzed nitro aldol condensation[48] and the subsequent dehydration with dicyclohexylcarbodiimide in the presence of Cu(I) catalyst.[46] A colorless oil: IR 1645, 1600, 1530, 1355 cm^{-1}; ^{1}H NMR δ 2.4–2.9 (m, 4 H), 6.89 (br d, 1 H, J = 12 Hz), 7.05–7.4 (m, 6 H); MS m/e 177 (M$^+$). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.82; H, 6.25; N, 7.90.

General Procedure for the Reaction of Stannylallenes (1a and 1b) with α,β-Unsaturated Carbonyl Compounds (2) Giving β-Propargylic Ketones (3). Under a nitrogen atmosphere, a CH_2Cl_2 solution of $TiCl_4$ (1 M, 1.2 mL) was added to a solution of **2** (1.0 mmol) in anhydrous CH_2Cl_2 (2 mL) at −40 °C. After 10 min, a solution of **1** (2.0 mmol) in anhydrous CH_2Cl_2 (2 mL) was added, and the whole was stirred at the temperature and for the period of time given in Table I. The reaction was quenched with water (10 mL), and AcOEt (10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with AcOEt (10 mL). The combined organic layer was dried and concentrated in vacuo. The residue was diluted in ether (10 mL), and saturated aqueous KF (10 mL) was added. The mixture was vigorously stirred for 1 h, and the precipitates were filtered off. The organic layer was separated, and the aqueous layer was extracted with AcOEt (10 mL). The combined organic layer was washed with brine, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (AcOEt–*n*-hexane) to give **3**.

3-(2-Propynyl)cyclohexanone (3a). A colorless oil: bp 73–76 °C (9 Torr) (bath temperature); IR 3310, 2110, 1710 cm^{-1}; ^{1}H NMR δ 1.4–2.6 (m, 11 H), 2.03 (t, 1 H, J = 2.5 Hz); high-resolution MS calcd for $C_9H_{12}O$ (M$^+$) 136.0886, found 136.0885.

3-(3-Butyn-2-yl)cyclohexanone (3b). A colorless oil: IR 3310, 2120, 1710 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.181 and 1.215 (d each in 1.1:1 ratio, 3 H in total, J = 7.3 Hz each), 1.52–1.87 (m, 4 H), 2.01–2.14 (m, 1 H), 2.117 (d, 1 H, J = 2 Hz), 2.24–2.56 (m, 5 H); high-resolution MS calcd for $C_{10}H_{14}O$ (M$^+$) 150.1042, found 150.1040.

3-(2-Propynyl)cyclopentanone (3c). A colorless oil: IR 3310, 2110, 1720 cm^{-1}; ^{1}H NMR δ 1.5–2.5 (m, 9 H), 2.03 (t, 1 H, J = 2.5 Hz); high-resolution MS calcd for $C_8H_{10}O$ (M$^+$) 122.0729, found 122.0729.

3-(2-Propynyl)cycloheptanone (3d). A colorless oil: bp 76–80 °C (9 Torr) (bath temperature); IR 3220, 2120, 1695 cm^{-1}; ^{1}H NMR δ 1.2–2.7 (m, 13 H), 2.01 (t, 1 H, J = 2.5 Hz); high-resolution MS calcd for $C_{10}H_{14}O$ (M$^+$) 150.1043, found 150.1038.

2-Methyl-5-(1-propen-2-yl)-3-(2-propynyl)cyclohexanone (3e). A colorless oil: bp 81–85 °C (0.5 Torr) (bath temperature); IR 3310, 2110, 1705, 1640 (sh) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.028, 1.058, and 1.088 (d each, 3 H in total, J = 6.7 Hz each), 1.992 (t, J = 2.5 Hz) in 1.74–2.09 (m, 6 H), 2.28–2.74 (m, 7 H), 4.690, 4.759, 4.808, and 4.853 (br s each in 1:2.5:2.5:1 ratio, 2 H in total); MS m/e 190 (M$^+$). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.77; H, 9.81.

3-(3-Butyn-2-yl)-2-methyl-5-(1-propen-2-yl)cyclohexanone (3f). A colorless oil: bp 90–95 °C (0.7 Torr) (bath temperature); IR 3310, 2110, 1700, 1640 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.08–1.28 (m, 6 H), 1.70–2.11 (m, 7 H), 2.34–3.02 (m, 5 H), 4.72–4.89 (m, 2 H); high-resolution MS calcd for $C_{14}H_{20}O$ (M$^+$) 204.1514, found 204.1514.

3-Phenyl-5-(2-propynyl)cyclohexanone (3g). Colorless crystals: mp 95–97 °C; IR 3310, 2110, 1710, 1600 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.011 (t, J = 2.5 Hz) in 2.01–2.39 (m, 7 H), 2.57–2.71 (m, 3 H), 3.406 (m, 1 H, $W_{1/2}$ = 17 Hz), 7.20–7.33 (m, 5 H); high-resolution MS calcd for $C_{15}H_{16}O$ (M$^+$) 212.1201, found 212.1211.

1,3-Diphenyl-5-hexynone (3h). Colorless crystals: mp 58–59 °C (*n*-hexane); IR 3320, 2120, 1685, 1600, 1580 cm^{-1}; ^{1}H NMR

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(48) Wollenberg, R. H.; Miller, S. J. *Tetrahedron Lett.* **1978**, 3219.

δ 1.96 (t, 1 H, J = 2.5 Hz), 2.61 (dd, 2 H, J = 6, 2.5 Hz), 3.15–3.75 (m, 3 H), 7.15–7.6 (m, 8 H), 7.90 (dd, 2 H, J = 8, 2 Hz); MS m/e 248 (M^+). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.04; H, 6.47.

4-Methyl-1,3-diphenyl-5-hexynone (3i). A colorless oil: IR 3310, 2110, 1680, 1595, 1580 cm^{-1}; ^1H NMR (500 MHz) δ 1.082 (d, 3 H, J = 6.7 Hz), 2.136 and 2.176 (d each in 1:1.2 ratio, 1 H in total, J = 2.4 Hz each), 2.73–2.80 and 2.98–3.04 (m each in 1.2:1 ratio, 1 H in total), 3.34–3.49 (m, 2 H), 3.64–3.75 (m, 1 H), 7.15–7.56 (m, 8 H), 7.889 and 7.965 (dd each in 1.2:1 ratio, 2 H in total, J = 8, 1.5 Hz each); high-resolution MS calcd for $C_{19}H_{18}O$ (M^+) 262.1358, found 262.1365.

4-Phenyl-6-heptyn-2-one (3j). A colorless oil: IR 3310, 2110, 1710, 1600 cm^{-1}; ^1H NMR (500 MHz) δ 1.985 (t, 1 H, J = 2.5 Hz), 2.086 (s, 3 H), 2.482 (ddd, 1 H, J = 16.7, 7, 2.5 Hz), 2.559 (ddd, 1 H, J = 16.7, 7, 2.5 Hz), 2.819 (dd, 1 H, J = 17, 7 Hz), 3.036 (dd, 1 H, J = 17, 7 Hz), 3.412 (quintet, 1 H, J = 7 Hz), 7.20–7.32 (m, 5 H); MS m/e 186 (M^+). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.64; H, 7.45.

1-Acetyl-2-(2-propynyl)cyclohexane (3k). A colorless oil: bp 60–65 °C (0.6 Torr) (bath temperature); IR 3310, 2110, 1705 cm^{-1}; ^1H NMR (500 MHz) δ 1.25–2.17 (m, $^7/_7$ H), 1.955 (t, 1 H, J = 2.4 Hz), 2.159 and 2.181 (s each in 6:1 ratio, 3 H in total), 2.260 (ddd, $^6/_7$ H, J = 17, 8.5, 2.4 Hz), 2.476 (td, $^1/_7$ H, J = 10.5, 3.5 Hz), 2.819 (dt, $^6/_7$ H, J = 7.5, 3.7 Hz); MS m/e 164 (M^+). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.24; H, 10.05.

3,3-Dimethyl-1-phenyl-5-hexynone (3l). Colorless crystals: mp 50–51 °C (n-hexane); IR 3300, 2110, 1685, 1670, 1595, 1580 cm^{-1}; ^1H NMR δ 1.13 (s, 6 H), 1.99 (t, 1 H, J = 2.5 Hz), 2.33 (d, 2 H, J = 2.5 Hz), 2.96 (s, 2 H), 7.2–7.5 (m, 3 H), 7.88 (dd, 2 H, J = 8, 2 Hz); MS m/e 200 (M^+). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.00; H, 8.11.

General Procedure for the Reaction of Stannylallenes (1c and 1d) with α-Nitro Olefins (4). (a) Preparation of β-Propargylic Nitroalkanes (5a–d) from 4a or 4b (Procedure A). Under a nitrogen atmosphere, to a mixture of **1** (1 mmol) and **4** (0.5 mmol) in anhydrous CH_2Cl_2 (3 mL) was added a CH_2Cl_2 solution of $TiCl_4$ (1 M, 0.6 mL) at −78 °C. The reaction mixture was stirred at the same temperature for 10–40 min, and water (5 mL) and ether (5 mL) were added. The whole was stirred at room temperature for 30 min, and the organic layer was separated. The aqueous layer was extracted with ether (5 mL), and the combined organic layer was dried and concentrated in vacuo. The residue was treated with aqueous KF and purified similarly as described for the preparation of **3** to give **5**.

(b) Preparation of α-Propargylic Ketones (6a–g) from 4c–f (Procedure B). Similarly as described in procedure A, **1** (1 mmol) and **4** (0.5 mmol) were treated with $TiCl_4$ (0.6 mmol) in anhydrous CH_2Cl_2 at −78 °C for 10–40 min and subjected to usual workup. The crude product was treated with 3 N HCl (5 mL) in THF (5 mL) at room temperature (for entries 5, 9–11) or at reflux (for entries 6–8) for several hours (until the more polar product turned into another, which was monitored by TLC). Ether (5 mL) was added, and the organic layer was separated. The aqueous layer was extracted with ether (5 mL), and the combined organic layer was washed with brine, dried, and concentrated in vacuo. The residue was treated with aqueous KF and purified similarly as described for the preparation of **3** to give **6**.

5-Nitro-4-phenyl-1-pentyne (5a). A pale yellow oil: IR 3320, 2130, 1605, 1560, 1380 cm^{-1}; ^1H NMR (500 MHz) δ 2.094 (t, 1 H, J = 2.4 Hz), 2.597 (ddd, 1 H, J = 17.1, 7.2, 2.4 Hz), 2.674 (ddd, 1 H, J = 17.1, 7.2, 2.4 Hz), 3.724 (quintet, 1 H, J = 7.2 Hz), 4.681 (dd, 1 H, J = 12.8, 7.2 Hz), 4.887 (dd, 1 H, J = 12.8, 7.2 Hz), 7.25–7.38 (m, 5 H); MS m/e 189 (M^+). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.55; H, 5.74; N, 7.47.

3-Methyl-5-nitro-4-phenyl-1-pentyne (5b). A pale yellow oil: IR 3300, 1600, 1555, 1375 cm^{-1}; ^1H NMR (500 MHz) δ 1.071 and 1.099 (d each in 1:1 ratio, 3 H, in total, J = 6.7 Hz each), 2.223 and 2.270 (d each in 1:1 ratio, 1 H in total, J = 2.5 Hz each), 2.730 (m, $^1/_2$ H, $W_{1/2}$ = 33 Hz), 2.964 (m, $^1/_2$ H, $W_{1/2}$ = 28 Hz), 3.418 (td, $^1/_2$ H, J = 10, 4.5 Hz), 3.544 (td, $^1/_2$ H, J = 7.5, 5.5 Hz), 4.726 (dd, $^1/_2$ H, J = 13, 10 Hz), 4.795 (dd, $^1/_2$ H, J = 13, 7.5 Hz), 4.911 (dd, $^1/_2$ H, J = 13, 7.5 Hz), 5.083 (dd, $^1/_2$ H, J = 13, 4.5 Hz), 7.19–7.34 (m, 5 H); high-resolution MS calcd for $C_{12}H_{13}NO_2$ (M^+) 203.0947, found 203.0964.

4-(Nitromethyl)-6-phenyl-1-hexyne (5c). A pale yellow oil: IR 3320, 2120, 1600, 1550, 1380 cm^{-1}; ^1H NMR (500 MHz) δ 1.74–1.87 (m, 2 H), 2.068 (t, 1 H, J = 2.4 Hz), 2.41–2.46 (m, 3 H), 2.61–2.67 (m, 1 H), 2.71–2.77 (m, 1 H), 4.415 (dd, 1 H, J = 12.5, 6.4 Hz), 4.541 (dd, 1 H, J = 12.5, 6.4 Hz), 7.17–7.31 (m, 5 H); MS m/e 217 (M^+). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.72; H, 7.06; N, 6.50.

3-Methyl-4-(nitromethyl)-6-phenyl-1-hexyne (5d). A pale yellow oil: IR 3300, 1600, 1555, 1380 cm^{-1}; ^1H NMR (500 MHz) δ 1.195 and 1.245 (d each in 2.4:1 ratio, 3 H in total, J = 6.7 Hz each), 1.66–1.79 (m, 1 H), 1.87–1.95 (m, 1 H), 2.111 and 2.129 (d each in 2.4:1 ratio, 1 H, J = 2.4 Hz), 2.27–2.36 (m, 1 H), 2.59–2.80 (m, 3 H), 4.39–4.44 (m, 1 H), 4.55–4.60 (m, 1 H), 7.16–7.32 (m, 5 H); high-resolution MS calcd for $C_{14}H_{17}NO_2$ (M^+) 231.1256, found 231.1231.

3-Phenyl-5-hexyn-2-one (6a). A colorless oil: bp 91–95 °C (2 Torr) (bath temperature) [lit.[49] bp 78–81 °C (2 Torr)]; IR 3320, 2130, 1715, 1600 cm^{-1}; ^1H NMR δ 1.88 (t, 1 H, J = 2.5 Hz), 2.07 (s, 3 H), 2.50 (ddd, 1 H, J = 17, 7, 2.5 Hz), 2.91 (ddd, 1 H, J = 17, 7, 2.5 Hz), 3.86 (t, 1 H, J = 7 Hz), 7.15–7.35 (m, 5 H); MS m/e 172 (M^+).

4-Methyl-3-phenyl-5-hexyn-2-one (6b). A colorless oil: IR 3300, 2110, 1715, 1600 cm^{-1}; ^1H NMR (500 MHz) δ 0.951 and 1.242 (d each in 1:1.6 ratio, 3 H in total, J = 6.7 Hz each), 1.884 and 2.089 (d each in 1.6:1 ratio, 1 H in total, J = 2.4 Hz each), 2.088 and 2.145 (s each in 1.6:1 ratio, 3 H in total), 3.168 (dqd, $^5/_{13}$ H, J = 10.4, 6.7, 2.4 Hz), 3.295 (dqd, $^8/_{13}$ H, J = 9.8, 6.7, 2.4 Hz), 3.617 (d, $^8/_{13}$ H, J = 9.8 Hz), 3.709 (d, $^5/_{13}$ H, J = 10.4 Hz), 7.22–7.36 (m, 5 H); high-resolution MS calcd for $C_{13}H_{14}O$ (M^+) 186.1042, found 186.1022.

1-Decyn-5-one (6c). A colorless oil: bp 84–86 °C (15 Torr) (bath temperature) [lit.[50] bp 103 °C (18 Torr)]; IR 3310, 2120, 1710 cm^{-1}; ^1H NMR (500 MHz) δ 0.890 (t, 3 H, J = 7 Hz), 1.23–1.36 (m, 4 H), 1.55–1.62 (m, 2 H), 1.939 (t, 1 H, J = 2.4 Hz), 2.417 (t, 2 H, J = 7.3 Hz), 2.446 (dt, 2 H, J = 7.3, 2.4 Hz), 2.654 (t, 2 H, J = 7.3 Hz); MS m/e 152 (M^+).

1-Undecyn-5-one (6d). A colorless oil: bp 71 °C (0.6 Torr) [lit.[51] bp 98–100 °C (3 Torr)]; IR 3310, 2110, 1710 cm^{-1}; ^1H NMR δ 0.86 (t, 3 H, J = 6 Hz), 1.1–1.7 (m, 8 H), 1.93 (t, 1 H, J = 2.5 Hz), 2.3–2.8 (m, 6 H); MS m/e 166 (M^+).

3-Methyl-1-undecyn-5-one (6e). A colorless oil: IR 3300, 2100, 1710 cm^{-1}; ^1H NMR (500 MHz) δ 0.880 (t, 3 H, J = 7 Hz), 1.195 (d, 3 H, J = 7 Hz), 1.26–1.33 (m, 6 H), 1.53–1.61 (m, 2 H), 2.031 (d, 1 H, J = 2.5 Hz), 2.412 (m, 2 H, $W_{1/2}$ = 18 Hz), 2.476 (dd, 1 H, J = 17, 7 Hz), 2.669 (dd, 1 H, J = 17, 7 Hz), 2.983 (sextet d, 1 H, J = 7, 2.5 Hz); high-resolution MS calcd for $C_{12}H_{20}O$ (M^+) 108.1511, found 180.1495.

2-(2-Propynyl)cyclohexanone (6f). A colorless oil: bp 92–96 °C (12 Torr) (bath temperature) [lit.[52] bp 93–95 °C (12 Torr)]; IR 3320, 2120, 1710 cm^{-1}; ^1H NMR δ 1.95 (t, 1 H, J = 2.5 Hz), 1.4–2.8 (m, 11 H); MS m/e 136 (M^+).

2-(3-Butyn-2-yl)cyclohexanone (6g). A colorless oil: IR 3310, 2120, 1710 cm^{-1}; ^1H NMR (500 MHz) δ 1.160 and 1.196 (d each in 1:3 ratio, 3 H in total, J = 7 Hz each), 1.57–1.73 (m, 3 H), 1.91–1.97 (m, 1 H), 2.01–2.09 (m, 1 H), 2.020 and 2.058 (d each in 1:3 ratio, 1 H in total, J = 2.5 Hz each), 2.17–2.50 (m, 4 H), 3.01–3.05 (m, 1 H); high-resolution MS calcd for $C_{10}H_{14}O$ (M^+) 150.1042, found 150.1039.

5-Nitro-4-phenyl-2-pentanone (7). A mixture of **5a** (72 mg, 0.38 mmol), yellow HgO (205 mg, 0.9 mmol), and 20% H_2SO_4 (5 mL) in THF (15 mL) was heated at reflux for 30 min. After cooling, 0.5% HCl (20 mL) was added, and the whole was stirred for 10 min and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was washed with brine, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (1:2 AcOEt–n-hexane) to give an 83% yield (65 mg) of **7** as colorless crystals: mp 100.5–101 °C (benzene–n-hexane); IR 1720, 1550, 1375 cm^{-1}; ^1H NMR (500 MHz) δ 2.121 (s, 3 H), 2.921 (d, 2 H, J = 7.3 Hz), 4.008 (quintet, 1 H, J = 7.3 Hz), 4.605 (dd, 1 H, J = 12.2, 7.3 Hz), 4.693 (dd, 1 H, J = 12.2, 7.3 Hz), 7.21–7.36

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(m, 5 H); MS *m/e* 207 (M^+). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.60; H, 6.34; N, 6.66.

2-Phenyl-4-pentynal (8). Under a nitrogen atmosphere, NaOMe (27 mg, 0.5 mmol) was added to a solution of **5a** (95 mg, 0.5 mmol) in MeOH (1 mL). A solution prepared by adding NH_4OAc (0.93 g, 12 mmol) in water (3 mL) to 20% aqueous $TiCl_3$ (0.6 mL, 2 mmol) under a nitrogen atmosphere was then added. After being stirred at room temperature for 1 h, the reaction mixture was poured into ether (10 mL), and the organic layer was separated. The aqueous layer was extracted with ether (5 × 10 mL), and the combined organic layer was successively washed with 5% $NaHCO_3$ (10 mL) and brine (10 mL), dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (1:7 AcOEt–*n*-hexane) to give a 71% yield (56 mg) of **8** as a colorless oil: IR 3310, 2120, 1725, 1600 cm^{-1}; ^1H NMR δ 1.93 (t, 1 H, J = 2.5 Hz), 2.58 (ddd, 1 H, J = 17, 7.5, 2.5 Hz), 2.95 (ddd, 1 H, J = 17, 7.5, 2.5 Hz), 3.77 (t, 1 H, J = 7.5 Hz), 7.1–7.4 (m, 5 H), 9.82 (s, 1 H); high-resolution MS calcd for $C_{11}H_{10}O$ (M^+) 158.0732, found 158.0735.

2,5-Undecanedione (9). A mixture of **6e** (0.28 g, 1.7 mmol), yellow HgO (0.87 g, 4.1 mmol), and 20% H_2SO_4 (23 mL) in THF (23 mL) was heated at reflux for 15 min. The reaction mixture was worked up and purified similarly as described for the preparation of **7** to give a 61% yield (193 mg) of **9** as colorless crystals: mp 30.5–31.5 °C (*n*-hexane) (lit.[53] mp 33–34 °C); IR 1710 cm^{-1}; ^1H NMR δ 0.86 (t like, 3 H, J = 6 Hz), 1.2–1.7 (m, 8 H), 2.18 (s, 3 H), 2.45 (t, 2 H, J = 7.5 Hz), 2.68 (s, 4 H); MS *m/e* 184 (M^+).

Dihydrojasmone (10). To a solution of **9** (153 mg, 0.83 mmol) in EtOH (1.6 mL) was added 0.5 N NaOH (1.5 mL, 0.73 mmol), and the whole was heated at reflux for 1.5 h. After cooling, water (10 mL) and ether (10 mL) were added, and the organic layer was separated. The aqueous layer was extracted with ether (3 × 10 mL), and the combined organic layer was washed with brine, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (1:5 AcOEt–*n*-hexane) to give a 75% yield (103 mg) of **10** as a colorless oil: bp 95 °C (5 Torr) [lit.[53] bp 100–102 °C (6 Torr)]; IR 1690, 1640 cm^{-1}; ^1H NMR δ 0.86 (t like, 3 H, J = 6 Hz), 1.1–1.6 (m, 6 H), 2.04 (s, 3 H), 2.1–2.6 (m, 6 H); MS *m/e* 166 (M^+).

1-Hydroxy-2,5-undecanedione (11a). A Typical Procedure for the Transformation of 6 to 11. A mixture of **6e** (53 mg, 0.32 mmol), PIFA (550 mg, 1.28 mmol), and K_2CO_3 (66 mg, 0.48 mmol) was stirred in a mixed solvent (40:5:1 $CHCl_3$–CH_3CN–H_2O, 6 mL) at room temperature for 23 h. The reaction mixture was poured into a mixture of CH_2Cl_2 (3 mL) and water (7 mL), and the whole was stirred vigorously for 30 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 × 6 mL). The combined organic layer was dried and concentrated in vacuo. The residue was passed through a dry silica gel column with AcOEt as an eluent. The eluate was concentrated in vacuo and purified by column chromatography on silica gel (1:1 AcOEt–*n*-hexane) to give a 51% yield (33 mg) of **11a** as colorless crystals: mp 66–67 °C (*n*-hexane); IR 3600–3400, 1715 cm^{-1}; ^1H NMR (500 MHz) δ 0.881 (t like, 3 H, J = 7 Hz), 1.26–1.59 (m, 8 H), 2.447 (t, 2 H, J = 7 Hz), 2.627 (t, 2 H, J = 6 Hz), 2.813 (t, 2 H, J = 6 Hz), 4.333 (d, 2 H, J = 5 Hz); high-resolution MS calcd for $C_{11}H_{20}O_3$ (M^+) 200.1413, found 200.1414.

1-Hydroxy-3-methyl-2,5-undecanedione (11b) was obtained in 55% yield (25 mg) from **6f** (38 mg, 0.21 mmol) as a pale yellow oil: IR 3600–3400, 1715 cm^{-1}; ^1H NMR δ 0.86 (t like, 3 H, J = 6 Hz), 1.09 (d, 3 H, J = 8 Hz), 1.1–1.7 (m, 8 H), 2.3–3.2 (m, 5 H), 4.39 (s, 2 H); high-resolution MS calcd for $C_{12}H_{22}O_3$ (M^+) 214.1566, found 214.1565.

2-(3-Hydroxy-2-oxopropyl)cyclohexanone (11c) was obtained in 47% yield (129 mg) from **6g** (217 mg, 1.6 mmol) as a pale yellow oil: IR 3600–3300, 1715 (sh), 1705 cm^{-1}; ^1H NMR δ 1.2–2.5 (m, 8 H), 2.7–3.2 (m, 3 H), 4.29 (m, 2 H, $W_{1/2}$ = 10 Hz); high-resolution MS calcd for $C_9H_{14}O_3$ (M^+) 170.0943, found 170.0954.

3-Hexyl-2-hydroxy-2-cyclopentenone (12a). To a solution of **11a** (23.3 mg, 0.116 mmol) in MeOH (5 mL) was added 0.5 N NaOH (0.6 mL), and the mixture was heated at reflux for 1 h and concentrated in vacuo. To the residue were added CH_2Cl_2 (10 mL) and water (5 mL), and the mixture was acidified to pH 1–2 with 10% HCl under vigorous stirring and saturated with NaCl. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layer was washed with brine, dried, and concentrated in vacuo. The residue was purified by preparative TLC on silica gel (1:1 AcOEt–*n*-hexane) to give a 60% yield (12.6 mg) of **12a** as a pale yellow oil: IR 3600–3100, 1705, 1660 cm^{-1}; UV 259 nm; ^1H NMR δ 0.89 (t like, 3 H, J = 6 Hz), 1.15–1.7 (m, 10 H), 2.2–2.6 (m, 3 H); high-resolution MS calcd for $C_{11}H_{18}O_2$ (M^+) 182.1306, found 182.1296.

1-Hydroxy-3,3a,4,5,6,7-hexahydroinden-2-one (12b). Similarly as described for the preparation of **12a**, a 77% yield (32.5 mg) of **12b** was obtained from **11c** (47.2 mg, 0.28 mmol) as colorless crystals: mp 113–115 °C (benzene–*n*-hexane); IR 3500, 3500–3100, 1710, 1660 cm^{-1}; UV 261 nm; ^1H NMR (500 MHz) δ 1.029 (qd, 1 H, J = 12.5, 3.2 Hz), 1.28–1.38 (m, 1 H), 1.464 (qt, 1 H, J = 13, 3.5 Hz), 1.83–1.88 (m, 1 H), 1.93–1.98 (m, 2 H), 2.00–2.07 (m, 1 H), 2.13–2.17 (m, 1 H), 2.502 (br quintet, 1 H, J = 5.5 Hz), 2.582 (ddd, 1 H, J = 18.6, 6.5, 1.2 Hz), 2.961 (d quintet, 1 H, J = 14, 2.1 Hz); high-resolution MS calcd for $C_9H_{12}O_2$ (M^+) 152.0834, found 152.0823.

Supplementary Material Available: ^1H NMR spectra for compounds **3a–d,f,g,i**, **5b,d**, **6b,e,g**, **8**, **11a–c**, and **12a,b** (18 pages). Ordering information is given on any current masthead page.

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