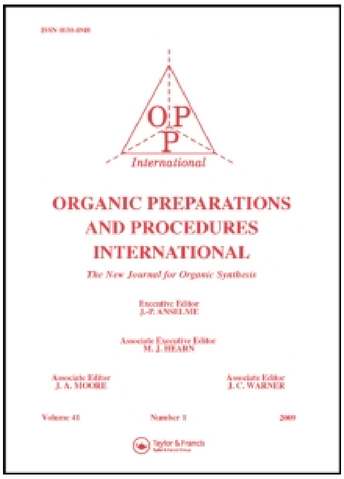

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SYNTHESES OF ω-ALKYNYL ALDEHYDES AND KETONES *via* OXIDATION OF ω-ALKYNYL ALCOHOLS WITH PYRIDINIUM DICHROMATE

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SYNTHESES OF ω-ALKYNYL ALDEHYDES AND KETONES *via* OXIDATION OF ω-ALKYNYL ALCOHOLS WITH PYRIDINIUM DICHROMATE

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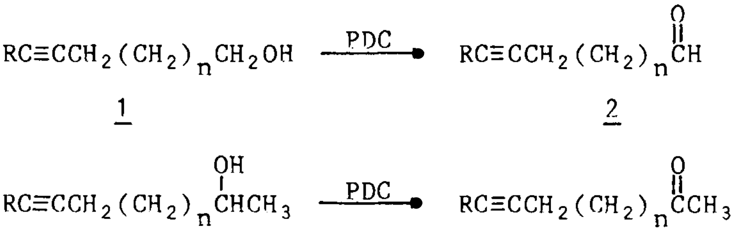
Pyridinium dichromate (PDC)[1] is an effective reagent for the oxidation of alcohols and a number of modifications of the original procedure have been reported.[2] Interestingly, PDC has never been used to oxidize non-conjugated acetylenic alcohols. As part of a project involving the synthesis of a number of unsaturated amino acids, we investigated the synthesis of a series of ω-alkynyl ketones and aldehydes. We now report that the PDC oxidation of ω-alkynyl alcohols is an effective route to the corresponding ω-alkynyl carbonyl compounds (Table I).



$$\underset{\mathbf{1}}{RC{\equiv}CCH_2(CH_2)_nCH_2OH} \xrightarrow{PDC} \underset{\mathbf{2}}{RC{\equiv}CCH_2(CH_2)_n\overset{O}{\overset{\|}{C}}H}$$

$$\underset{\mathbf{3}}{RC{\equiv}CCH_2(CH_2)_n\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow{PDC} \underset{\mathbf{4}}{RC{\equiv}CCH_2(CH_2)_n\overset{O}{\overset{\|}{C}}CH_3}$$

3 4

a) R = H, n = 1
b) R = H, n = 2
c) R = H, n = 7
d) R = $(CH_3)_3Si$-, n = 2
e) R = $(CH_3)_3Si$-, n = 7

Table I

OXIDATION OF ALKYNYL ALCOHOLS WITH PYRIDINIUM DICHROMATE

Product	Ratio of Alcohol:PDC	Isolated Yield	mp. of 2,4-DNP (°C)
2a	1:2	21%	132.5-133.5
2b	1:1.5	52%	102.5
2c	1:1.5	64%	85.5°
2d[a]	1:1.5	57%	109.5-110
2e[a]	1:2	63%	74.5-75.5
4b[b]	1:2[c]	80%	115-116
4c[b]	1:2[c]	81%	78.5-79.5
4e[b]	1:2[c]	84%	30-31

a) The starting alcohol was prepared by sequential treatment of the corresponding acetylenic alcohol with n-BuLi (2 equiv., -78°C), $(CH_3)_3SiCl$ (2 equiv., -78→0°), and HOAc (excess, 0→25°C).[3] b) The starting secondary alcohol was prepared by reaction of the corresponding aldehyde with CH_3MgI (1.05 equiv., 0°C). Removal of the trimethylsilyl protecting group was accomplished by sequential treatment with $AgNO_3$ (2.7 equiv.) and KCN (12.8 equiv.).[4] c) Oxidation of the secondary alcohol was performed in the presence of pyridinium trifluoroacetate (0.4 equiv).[1]

EXPERIMENTAL SECTION

The ^1H and ^{13}-NMR spectra were obtained on a JEOL-FX90Q spectrometer in $CDCl_3$ solutions using TMS as an internal standard. IR spectra were obtained on a Perkin-Elmer Model 1330 spectrometer. Melting points were recorded using a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed on each of the new ketones by Galbraith Laboratories, Knoxville, Tennessee. Elemental analyses were not generally performed on intermediate silyl alcohols and aldehydes since they were utilized to prepare ketones which were fully characterized.

Commercially available samples of 10-undecyn-1-ol (Wiley) 5-hexyn-1-ol (Farchan), 4-pentyn-1-ol (Farchan), n-butyllithium (Aldrich), chlorotrimethylsilane (Aldrich), pyridinium dichromate (Aldrich), methyl iodide (Aldrich), silver nitrate (Mallinckrodt), and potassium cyanide (Fisher) were used as received. Methylene chloride was distilled over P_2O_5 under nitrogen and stored over activated molecular sieve beads (4Å, Fisher). Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone. Glassware and equipment were oven-dried and flushed with nitrogen prior to use.

Protection of Terminal Alkynes. General Procedure. - The synthesis of 6-trimethylsilyl-5-hexyn-1-ol (1d) is representative. A 250 mL round bottomed flask equipped with a septum inlet, magnetic stirring bar, pressure equalizing addition funnel, and gas outlet (mercury bubbler) was assembled while hot, and then flushed with nitrogen while being flame-dried. The reaction flask was cooled to -78° under a stream of nitrogen and then *n*-butyllithium (20 mmol, 12.9 mL of a 1.55 M solution in hexane) was transferred into the reaction flask by means of a double-ended needle. Anhydrous THF (20 mL) was added to the flask by means of a syringe and the solution cooled to -78°C. A solution of 5-hexyn-1-ol (10 mmol, 0.98g) in anhydrous THF (10 mL) was transferred to the addition funnel, and added dropwise to the flask with stirring at -78° for 0.5 hr. Chlorotrimethylsilane (21 mmol, 2.66 mL) was then added dropwise, at -78°, and the mixture stirred for 2.5 hrs. During this period, the flask was allowed to gradually warm to 0°. Acetic acid (25%, 40 mL) was then added at 0°, and the mixture stirred at room temperature for 1 hr. The organic layer was separated and the aqueous layer extracted into ether (4x50 mL). The combined etheral layer was washed with conc.? aqueous HCl (50 mL) saturated aqueous sodium chloride (50 mL) and dried over anhydrous $MgSO_4$. Filtration, followed by evaporation of the solvent, gave a crude yellow oil. Purification by flash column chromatography (silica gel, 15% ethyl acetate-petroleum ether) afforded 1.65g (96%) of pure 1d as a colorless oil ^{1}H-NMR ($CDCl_3$): δ 4.42 (s, 1H, OH), (t, 2H, J=5.9 Hz, $\underline{CH_2}OH$), 2.26 (t, 2H, J=6.6 Hz, $\underline{CH_2}\text{-}C{\equiv}C$), 2.75-2.5 (m, 4H), 0.14 (s, 9H, $(CH_3)_3Si\text{-}$); ^{13}C-NMR ($CDCl_3$): δ 107.16 ($(CH_3)_3Si\text{-}\underline{C}{\equiv}C$), 84.71 ($(CH_3)_3Si\text{-}C{\equiv}\underline{C}$), 62.04 ($\underline{CH_2}OH$), 31.59, 24.88, 19.57 ($CH_2$'s) 0.12 ($(CH_3)_3Si\text{-}$); IR: 3340 cm^{-1} (br, OH), 2180 cm^{-1} (C≡C).

11-Trimethylsilyl-10-undecyn-1-ol (1e). - Treatment of 10-undecyn-1-ol (25 mmol, 4.21g) with *n*-butyllithium (50 mmol, 32.3 mL of a 1.55 M solution) at -78°, followed by successive treatment with chlorotrimethylsilane (52.5 mmol, 6.7 mL) and acetic acid (25%, 20 mL) gave 5.98g (99%) of 1e as a colorless oil after purification by flash column chromatography (silica gel, 10% ethyl acetate-petroleum ether). ^{1}H-NMR ($CDCl_3$): δ 3.62 (t, 2H, J=6.4 Hz, CH_2OH), 2.20 (t, 2H, J=6.4 Hz, CH_2-C≡C-), 1.81 (s, 1H, OH), 1.31 (m, 14H), 0.14 (s, 9H, $(CH_3)_3Si$-); ^{13}C-NMR ($CDCl_3$): δ 107.76 ($(CH_3)_3Si\underline{C}$≡C), 84.31 ($(CH_3)_3Si$-C≡$\underline{C}$-), 62.96 (CH_2OH), 32.81, 29.48, 29.40, 29.05, 28.80, 28.64, 25.77, 19.87 (CH_2's), 0.21 ($(CH_3)_3Si$-); IR (neat): 3340 cm^{-1} (br, OH), 2180 cm^{-1} (C≡C).

Oxidation of Primary Alkynyl Alcohols. General Procedure[1]. - The synthesis of 11-trimethylsilyl-10-undecynal (2e) is representative. To an oven-dried 250 mL round-bottomed flask fitted with a septum inlet was added freshly ground pyridinium dichromate (PDC, 63.46 mmol, 23.87g). The flask was equipped with a magnetic stirring bar, reflux condenser, and a gas outlet (mercury bubbler). The apparatus was assembled while hot, purged with nitrogen while being flame-dried, and allowed to come to room temperature under a stream of nitrogen. Anhydrous methylene chloride (60 mL) was added to the flask, followed by a solution of 11-trimethylsilyl-10-undecyn-1-ol (31.73 mmol, 7.63g) dissolved in anhydrous methylene chloride (5 mL). The mixture was stirred at room temperature for 20 hrs, during which time the reaction mixture became dark and thick. It was diluted with ether (50 mL) and the liquid layer decanted. The tarry residue was washed repeatedly with ether (50 mL portions) until the residue became powdery. The combined etheral washings were then filtered through a short column of silica gel to remove insoluble chromium by-products. Evaporation of the solvent, and by purification by column chromatography (silica gel, 5% ethyl acetate-petroleum ether) gave 4.80g (63%) of 2e as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 9.76 (t, 1H, J=1.75 Hz, CHO), 2.43 (t, 2H, J=6.5 Hz, CH_2CHO), 2.21 (t, 2H, J=6.4 Hz, CH_2-C≡C), 1.32 (m, 12H), 0.14 (s, 9H, $(CH_3)_3Si$); ^{13}C-NMR ($CDCl_3$): δ 202.81 (CHO), 107.65 ($(CH_3)_3Si$-$\underline{C}$≡C-), 84.33

($(CH_3)_3Si-C{\equiv}\underline{C}-R$), 43.92 ($\underline{CH_2}CHO$), 29.21, 29.10, 28.86, 28.70, 28.59, 22.09, 19.84 (CH_2's), 0.23 ($(CH_3)_3Si$); IR (neat) 2932 cm^{-1} (CH_2's), 2862 cm^{-1}, 2722 cm^{-1} (CHO), 2185 cm^{-1} ($C{\equiv}C$), 1730 cm^{-1} (C=O), 1243 cm^{-1}, 845 cm^{-1}, 767 cm^{-1}

2,4-DNP, mp., 74.5-75.5°.

Anal. Calcd. for $C_{20}H_{30}N_4O_4Si$: C, 57.39; H, 7.22, N, 13.39; Si, 6.71 Found: C, 57.22; H, 7.25; N, 13.41; Si, 6.39

6-Trimethylsilyl-5-hexynal (2d). - Treatment of 6-trimethylsilyl-5-hexyn-1-ol (5.93 mmol, 1.00g) with PDC (9.0 mmol, 3.39g) in anhydrous methylene chloride (8.5 mL) gave 0.57g (57%) of *2d* as a colorless oil after column chromatography (silica gel, methylene chloride). ^1H-NMR ($CDCl_3$): δ 9.80 (t, 1H, J=1.3 Hz, CHO), 2.59 (t, 2H, J=7.0 Hz, $\underline{CH_2}CHO$), 2.30 (t, 2H, J=6.8 Hz, $\underline{CH_2}-C{\equiv}C$), 1.83 (m, 2H, CH_2), 0.14 (s, 9H, $(CH_3)_3Si$); ^{13}C-NMR ($CDCl_3$): δ 201.73 (CHO), 105.87 ($(CH_3)_3Si-\underline{C}{\equiv}C-R$), 85.77 ($(CH_3)_3Si-C{\equiv}\underline{C}-R$), 42.65 ($\underline{CH_2}CHO$), 21.00, 19.21 ($CH_2$'s) 0.07 ($(CH_3)_3Si$)); IR (neat): 2920 cm^{-1} (CH_2), 2860 cm^{-1}, 2760 cm^{-1} (CHO), 2178 cm^{-1} ($C{\equiv}C$), 1730 cm^{-1} (C=O), 1245 cm^{-1}, 848 cm^{-1}, 768 cm^{-1}.

2,4-DNP derivative, mp. 109.5-110°.

10-Undecynal (2c). - Reaction of 10-undecyn-1-ol (50 mmol, 8.41g) with PDC (75 mmol, 28.2g) in anhydrous methylene chloride (75 mL) gave 5.32g (64%) of *2c* as a colorless oil after column chromatography (silica gel, 5% ethyl acetate-petroleum ether). ^1H-NMR ($CDCl_3$): δ 9.75 (t, 1H, J=1.75 Hz, CHO), 2.42 (t, 2H, J=7.2 Hz, $\underline{CH_2}CHO$), 2.16 (t, 2H, $\underline{CH_2}-C{\equiv}C$), 1.97 (t, 1H, J=2.8 Hz, $\underline{H}-C{\equiv}C$), 1.93 (m, 12H); ^{13}C-NMR ($CDCl_3$): δ 202.87 (CHO), 84.66 ($H-C{\equiv}\underline{C}-R$), 68.16 ($H-\underline{C}{\equiv}C-R$), 43.89 ($\underline{CH_2}CHO$), 29.21, 29.10, 28.89, 28.64, 28.42, 22.06, 18.38 (CH_2's); IR (neat): 3295 cm^{-1} ($C{\equiv}C-H$), 2840 cm^{-1}, 2720 cm^{-1} (CHO), 2120 cm^{-1} ($C{\equiv}C$), 1718 cm^{-1} (C=O).

2,4-DNP derivative, mp. 85.5°, lit.[5] 86°.

5-Hexynal (2b). - Reaction of 5-hexyn-1-ol (20 mmol, 1.96g) with PDC dichromate (30 mmol, 11.29g) in anhydrous methylene chloride (30 mL) gave 1.0g (52%) of *2b* as a colorless oil after column chromatography (silica gel, 10% ethyl acetate-petroleum ether). ^1H-NMR ($CDCl_3$): δ 9.80 (t, 1H, J=1.3 Hz,

CHO), 2.63 (t, 2H, J=7.0 Hz, $\underline{CH_2}$CHO), 2.28 (t, 2H, J=6.8 Hz, C≡C-$\underline{CH_2}$), 2.0-1.7 (m, 3H, CH$_2$, H-C≡C) ^{13}C-NMR (CDCl$_3$): δ 201.73 (C=O), 83.17 (H-C≡$\underline{C}$-R), 69.38 (H-$\underline{C}$≡C-R), 42.54 ($\underline{CH_2}$CHO), 20.84, 17.78 (CH$_2$'s); IR (neat): 3295 cm^{-1} (H-C≡C), 2920 cm^{-1} (CH$_2$), 2840 cm^{-1}, 2740 cm^{-1} (CHO), 2130 cm^{-1} (C≡C), 1725 cm^{-1} (C=O), 1112 cm^{-1}, 906 cm^{-1}, 845 cm^{-1}.
2,4-DNP derivative, mp. 102.5°, lit.[6] 90-91°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.28
Found: C, 51.71; H, 4.46; N, 19.94

4-Pentynal (2a). - 4-Pentyn-1-ol (297.2 mmol, 25.0g) was treated with PDC (594 mmol, 223.6g) in anhydrous methylene chloride (500 mL). After 20 hrs, the mixture was diluted with ether (100 mL) and the liquid layer decanted off. The tarry residue was washed repeatedly with ether (100 mL portions) until the residue became granular. The combined ethereal fractions were filtered through a short silica gel column to yield a light brown oil. Purification by column chromatography (silica gel, methylene chloride), removal of the solvent by fractional distillation using a 40 cm packed glass bead column, and final distillation of the product (40°, 20 torr) gave 5.02g (21%) of **2a** as a colorless oil. ^{1}H-NMR (CDCl$_3$): 9.80 (t, 1H, J=1.8 Hz, CHO), 3.0-2.4 (m, 4H), 1.97 (t, 1H, J=2.8 Hz, $\underline{H}$-C≡C); ^{13}C-NMR (CDCl$_3$): δ 200.08 (CHO), 82.33 (H-C≡$\underline{C}$-R), 69.25 (H-$\underline{C}$≡C-R), 42.21 ($\underline{CH_2}$CHO), 11.55 (H-C≡C-$\underline{CH_2}$); IR (neat): 3292 cm^{-1} (H-C≡C-), 2920 cm^{-1} (CH$_2$) 2840 cm^{-1}, 2740 cm^{-1} (CHO), 2130 cm^{-1} (C≡C), 1725 cm^{-1} (C=O).
2,4-DNP, mp. 132.5-133.5°, lit.[7] 130°.

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.38; H, 3.84; N, 21.36
Found: C, 50.39; H, 3.88; N, 21.26

Preparation of Secondary Alcohols. *General Procedure*. - The synthesis of 11-dodecyn-2-ol (**3c**) is representative. Magnesium turnings (19.1 mmol, 0.47g) were placed in an oven-dried, 100 mL round bottomed flask fitted with a septum inlet. The flask was equipped with a magnetic stirring bar, Claisen head adapter, addition funnel, and Dry Ice condenser. The apparatus was assembled hot, flame dried, purged with nitrogen, and allowed to cool under a stream of nitrogen. An iodine crystal was added and the system flushed with nitrogen. The condenser was cooled to -78°, and anhydrous ether (25 mL) added to the flask. Methyl iodide (20 mmol, 1.25 mL) was added and the mixture stirred at room temperature until the magnesium dissolved (~30 minutes). The reaction flask was cooled to 0°, and then a solution of 11-trimethylsilyl-10-undecynal (17.74 mmol, 4.23g) in anhydrous ethyl ether (10 mL) was transferred to the addition funnel and added dropwise to the reaction mixture. After the addition, the mixture was stirred at 0° for 3 hrs. Water (10 mL) and conc. HCl (5 mL) were then added sequentially (dropwise) to the mixture at 0°, and stirring was continued until all of the precipitate had dissolved. The ether layer was separated, and the aqueous layer extracted with ether (3x25 mL). The combined ethereal extracts were washed sequentially with a sodium thiosulfate solution (5%, 25 mL) and water (25 mL), and then dried over anhydrous magnesium sulfate. Filtration, followed by removal of the solvent gave 4.5g of a yellow oil. The crude alcohol was dissolved in ethanol (40 mL) and placed in a 500 mL round-bottomed flask equipped with a magnetic stirring bar and an addition funnel. A 0.66 M solution of silver nitrate (47.9 mmol, 8.13g in 72 mL of 1:3 H_2O-EtOH) was placed in the addition funnel and added dropwise at room temperature over a 15 minute period. The mixture was stirred at 50°C for 1.5 hours, during which time a black precipitate formed. Potassium cyanide (240 mmol, 15.63g) was added dropwise as a 10 M aqueous solution at 50°C, and stirred until all the precipitate had dissolved. The reaction mixture was extracted with ether (5x100 mL) and the combined ether extracts dried ($MgSO_4$). Filtration and evaporation of the solvent gave the crude alcohol. Purification by chromatography (silica gel, 20% ethyl acetate-petroleum ether) gave 2.95g (91% from <u>2e</u>) of <u>4c</u> as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 3.9-3.6 (m, 1H, $CH_2\underline{CH}(OH)CH_3$), 2.16 (m, 2H, $H\text{-}C{\equiv}C\text{-}\underline{CH_2}\text{-}R$), 1.94 (t, 1H, J=2.5 Hz, $\underline{H}\text{-}C{\equiv}C\text{-}R$), 1.75-1.0 (m, 18H, doublet shoulder at 1.21 and 1.14, J=6.2 Hz, is $-CH(OH)\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$): δ 84.81 ($H\text{-}C{\equiv}\underline{C}\text{-}R$), 68.20 ($R\underline{CH}(OH)CH_3$), 68.13 ($H\text{-}\underline{C}{\equiv}C\text{-}R$), 39.35, 29.60, 29.48, 29.06, 28.75, 28.49, 25.77, 23.48, 18.41; IR (neat): 3640-3060 cm^{-1} (b, OH), 3310 cm^{-1} ($H\text{-}C{\equiv}C$), 2963 cm^{-1} (CH_3), 2925 cm^{-1} (CH_2), 2860 cm^{-1} ($R_3C\text{-}H$), 2120 cm^{-1} ($C{\equiv}C$), 1345 cm^{-1}.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16
Found: C, 79.27; H, 11.82

6-Heptyn-2-ol (3b). - Treatment of methylmagnesium iodide [21.15 mmol, prepared by reaction of 21.15 mmol (0.52g) of magnesium turnings with methyl iodide (22.15 mmol, 3.14g) in anhydrous ether (10 mL)] with 6-trimethylsilyl-5-hexynal (20.14 mmol, 3.14g) dissolved in anhydrous ether (10 mL) gave 3.71g of a yellow oil. The crude alcohol dissolved in 50 mL of ethanol was treated successively with silver nitrate (54.38 mmol, 9.24g, 0.66 *M* in 1:3 H_2O-EtOH) and with potassium cyanide (257.8 mmol, 16.79g, 10 *M* in H_2O) at 50°. Purification by flash chromatography (silica gel, 10% ethyl acetate-petroleum ether) gave 1.53g (68% from *2d*) of *4b* as a colorless oil; bp. 185°, lit.[8] 75-77°/12 torr. ^{1}H-NMR ($CDCl_3$): δ 4.0-3.65 (m, 1H, $CH_2\underline{CH}(OH)CH_3$) 2.24 (m, 2H, $H\text{-}C{\equiv}C\text{-}\underline{CH_2}CH_2R$), 1.96 (t, 1H, J=2.6 Hz, $\underline{H}\text{-}C{\equiv}C\text{-}CH_2R$), 1.85 (s, 1H, OH), 1.60 (m, 4H, CH_2's), 1.24, 1.17 (d, 3H, J=6.2 Hz, CH_3); ^{13}C-NMR ($CDCl_3$): δ 84.39 ($H\text{-}C{\equiv}\underline{C}\text{-}R$), 68.57 ($H\text{-}\underline{C}{\equiv}C\text{-}R$), 67.64 ($R_2\underline{CH}OH$), 38.20 ($\text{-}CH_2\underline{CH_2}CH_2\text{-}$), 24.71 ($R\underline{CH_2}CH(OH)CH_3$), 23.58 ($CH_3$), 18.40 ($H\text{-}C{\equiv}C\text{-}\underline{CH_2}\text{-}$); IR: 3690-3020 cm^{-1} (br, OH), 3305 cm^{-1} ($H\text{-}C{\equiv}C$), 2963 cm^{-1} (CH_3), 2925 cm^{-1} (CH_2).

Oxidation of Secondary Alkynyl Alcohols. *General Procedure*[1]. The synthesis of 11-dodecyn-2-one (4c) is representative. PDC (19.4 mmol, 7.30g) and pyridinium trifluoroacetate (3.89 mmol, 0.75g) were placed into an oven dried 100 mL round bottomed flask fitted with a septum inlet. The flask was equipped with a magnetic stirring bar, reflux condenser, and gas outlet to a mercury bubbler, assembled while hot, and allowed to cool under a stream of nitrogen. Anhydrous methylene chloride (20 mL) was introduced, followed by a solution of 11-dodecyn-2-ol (9.71 mmol, 1.77g) in anhydrous methylene chloride (5 mL). The mixture was stirred at room temperature for 20 hrs, and then diluted with ether (10 mL).

The liquid portion was decanted and the residue washed with ether until it became granular. The combined ether washings were then filtered through a short column of silica gel. Evaporation of the solvent gave 2.04g of the crude ketone. Purification by column chromatography (silica gel, 5% ethyl acetate-petroleum ether) afforded 1.42g (81%) of 4c as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 2.45 (t, 2H, J=6.8 Hz, $RCH_2(C{=}O)CH_3$), 2.3-2.0 (m, 4H), 1.96 (t, 1H, J=2.6 Hz, H-C≡C-CH_2R), 1.8-1.15 (m, 13H, CH_2's, CH_3); ^{13}C-NMR ($CDCl_3$): δ 209.10 (C=O), 84.60 (H-C≡C-R), 68.10 (H-C≡C-R), 43.70, 29.81, 29.24, 29.07, 28.89, 28.64, 28.42, 23.77, (CH_2's, CH_3) 18.35 (CH_2-C≡C-H); IR: 3295 cm^{-1} (H-C≡C-), 2932 cm^{-1} (CH_3), 2860 cm^{-1} (CH_2), 2125 cm^{-1} (C≡C), 1715 cm^{-1} (C=O), 1362 cm^{-1}, 1170 cm^{-1}.

2,4-DNP derivative, mp. 78.5-79.5°.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.99; H, 6.71; N, 15.54
Found: C, 59.73; H, 6.62; N, 15.42

6-Heptyn-2-one (4b). - Treatment of 6-heptyn-2-ol (6.42 mmol, 0.72g) with PDC (12.84 mmol, 4.83g) and pyridinium trifluoroacetate (2.57 mmol, 0.50g) in anhydrous methylene chloride (13 mL) gave 570 mg (80.3%) of 4b as a colorless oil after column chromatography (silica gel, methylene chloride). ^{1}H-NMR ($CDCl_3$): δ 2.60 (t, 2H, J=7.0 Hz, $RCH_2(C{=}O)CH_3$), 2.4-2.1 (m, 5H, with a singlet at 2.16 (3H, CH_3)), 2.0-1.6 (m, 3H, triplet centered at 1.96, J=2.6 Hz, is H-C≡C); ^{13}C-NMR ($CDCl_3$): δ 200.12 (C=O), 83.57 (H-C≡C-R), 69.05 (H-C≡C-R), 42.02, 30.05 (CH_3), 22.25, 17.75; IR: 3295 cm^{-1} (H-C≡C), 2940 cm^{-1}, 2125 cm^{-1} (C≡C), 1714 cm^{-1} (C=O), 1375 cm^{-1}, 1166 cm^{-1}.

2,4-DNP derivative, mp. 115-116°, lit.[9] 118-119°.

12-Trimethylsilyl-11-dodecyn-2-one (4e). - Treatment of 12-trimethylsilyl-11-dodecyn-2-ol (3.26 mmol, 0.83g) with PDC (6.8 mmol, 2.55g) and pyridinium trifluoroacetate (1.36 mmol, 260 mg) in anhydrous methylene chloride (6.4 mL) gave 690 mg (84%) of 4e as a colorless oil after column chromatography (silica gel, methylene chloride). ^{1}H-NMR ($CDCl_3$): δ 2.5-1.9 (m, 7H, contains triplet centered at 2.28 and a singlet at 1.99 (CH_3)), 1.7-1.0 (m, 12H), 0.03 (s, 9H, $(CH_3)_3Si$);

^{13}C-NMR ($CDCl_3$): δ 209.01 (C=O), 107.60 (($(CH_3)_3Si-\underline{C}\equiv C-R$), 84.20 ($(CH_3)_3Si-C\equiv\underline{C}-R$), 43.70, 29.78, 29.21, 29.05, 28.86, 28.64, 28.53, 23.76, 19.78, 0.15 ($(CH_3)_3Si$); IR (neat): 2371 cm^{-1} ($C\equiv C$), 1716 cm^{-1} (C=O), 1360 cm^{-1}, 1250 cm^{-1}, 1168 cm^{-1}, 840 cm^{-1}, 757 cm^{-1}, 698 cm^{-1}.

2,4-DNP derivative, mp. 30-31°.

Anal. Calcd. for $C_{21}H_{32}N_4O_4Si$: C, 58.31; H, 7.46; N, 12.95; Si, 6.49 Found: C, 58.35; H, 7.70; N, 13.11; Si, 4.87

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