Pergamon

Tetrahedron Letters, Vol. 35, No. 16, pp. 2553-2554, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0399-I

A Novel Stereoselective Synthesis of (*Z*)-3-Iodo-3-alken-1-one from 2-Alkyn-1-one

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Abstract: A one-pot reaction of 2-alkyn-1-one with sodium iodide/acetonitrile/trimethylsilyl chloride/water or trimethylsilyl iodide/acetonitrile at 25°C gave almost exclusively (*Z*)-3-iodo-3-alken-1-one in good yields.

The synthesis of stereoselective 3-halo-3-alken-1-ones is still a synthetic challenge. Recently, we reported

[redacted]

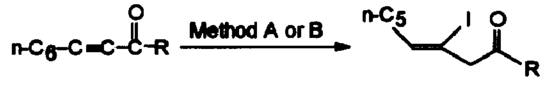
NOESY NMR spectral analysis. The results are summarized in Table 1.[illegible] In a typical procedure, CH_3CN (5 mL), TMSCl (0.55 g, 5 mmol), water (0.05 g, 2.5 mmol), and 3-decyn-2-one **1** (0.76 g, 5 mmol) were sequentially added into a dry flask containing NaI (0.75 g, 5 mmol) under nitrogen atmosphere at room temperature. After 2h, the reaction mixture was quenched with water, extracted with ether, concentrated, and chromatographed (silica gel, n-hexane/ether = 4/1) to give (*Z*)-4-iodo-4-decen-2-one **2**[4] in 85% yield. No great changes in the product yields were observed when we treated **1** with 1 equiv of 1,4-benzoquinone prior to run the reactions under either Method A or B conditions. Besides, using hexane instead of CH_3CN in the reaction, no reaction occurred. These results may rule out the possibility that both reactions involved a radical process. TMSCl was essential to this reaction. Without adding TMSCl to the reaction, only starting material **1** was recovered under the $NaI/CH_3CN/H_2O$ system. Water also played an important role in the $NaI/CH_3CN/TMSCl/H_2O$ system. In the absence of water, **1** was recovered in 76-83% after 3h in the reaction conditions of $TMSCl/NaI/CH_3CN$. Using excess of water in the $TMSCl/NaI/CH_3CN$ system, the products (*E*)-4-iodo-3-decen-2-one **3** and (*Z*)-4-iodo-3-decen-2-one **4** become increased (entries 2, 3, 4, and 5). When we treated heptadeca-7,10-diyn-9-one with 2 equiv of $NaI/TMSCl/H_2O$ in CH_3CN, only (*Z,Z*)-7,11-diiodoheptadeca-6,11-dien-9-one can be isolated in good yield (78%).

Treatment of **1** with $TMSI/CH_3CN$ at -25°C followed by the addition of benzaldehyde gave (*Z*)-3-(hydroxy-phenyl-methyl)-4-iodo-4-decen-2-one with 85% diastereoselectivity in 46% yield.[5] These results indicate that the first step in the mechanism (**Scheme I**) would be the formation of an iodo allenol silane **5**[6] by the 1,4-addition of iodide on to the silicon activated electrophilic oxygen. Acid catalyzed double bond migration in the intermediate **5** by the protonation of the central carbon of the allene and simultaneous deprotonation of the γ-carbon by an intermolecular base would give rise to the more stable dienyl silane **6**. Hydrolysis of **6** would result in the observed product **2**.

Acknowledgment

We thank the National Science Council and Academia Sinica of the Republic of China for financial support.

Table I. One-Pot Conversion of 2-Alkyn-1-one into (Z)-3-Iodo-3-alken-1-one.

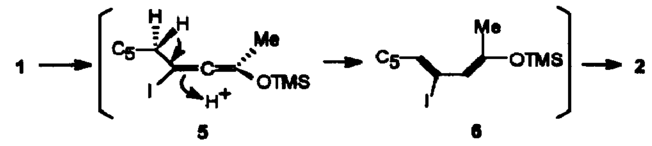


Method A: TMSCl/NaI/$\frac{1}{2}H_2O/CH_3CN$, B: TMSI/CH_3CN.

Entry	R =	Method	Iso. Yield (%)
1	Me-	A	85
2	Me-	A[a]	86[b]
3	Me-	A[c]	23[d]
4	Me-	A[e]	43[f]
5	Me-	A[g]	<1[h]
6	n-C_5-	A	81
7	Ph-	A	78
8	Me-	B	86
9	n-C_5-	B	83
10	Ph-	B	76
11	H-	A	75
12	H-	B	80

[a] Used 1 equiv of H_2O in this reaction. [b] By-product is 4 (4%). [c] Used 5 equiv of H_2O in this reaction. [d] By-products are 3 (17%) and 4 (40%). [e] Used 5 equiv of H_2O and 5 equiv of TMSCl in this reaction. [f] The other major product is (Z)-4-chloro-4-decen-2-one (43%). [g] Used 20 equiv of H_2O in this reaction. [h] Other compounds are 3 (26%), 4 (31%), (Z)-4-chloro-3-decen-2-one (14%), and (E)-4-chloro-3-decen-2-one (29%).

Scheme I. The Proposed Mechanism for the Formation of (Z)-4-Iodo-4-decen-2-one 2.



References and Notes

1. Luo, F. T.; Fwu, S. L.; Hwang, W. S. *Tetrahedron Lett.* **1992**, *33*, 6839.
2. The reaction of 1-phenyl-2-propynone with metal halides in acetic acid at room temperature gave *E/Z* mixture of 3-halo-2-alken-1-ones : Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709.
3. All new compounds have been fully characterized by ^1H- and ^{13}C-NMR, MS or IR spectroscopy, and either elemental analysis or high resolution mass spectroscopy.
4. (Z)-4-Iodo-4-decen-2-one 2. ^1H NMR ($CDCl_3$,TMS) δ 0.90 (t, J = 6.7 Hz, 3 H), 1.28-1.45 (m, 6 H), 2.14 (q with one singlet at δ 2.18, J = 6.8 Hz, 5 H), 3.70 (s, 2 H), 5.67 (t, J = 6.8 Hz, 1 H) ppm; ^{13}C-NMR ($CDCl_3$, TMS) δ 13.93, 22.34, 27.71, 29.26, 31.18, 36.51, 59.08, 95.89, 140.75, 204.89 ppm; IR (neat) 2959 (m), 2930 (m), 1708 (s), 1630 (w), 1580 (w), 1455 (w), 1410 (w), 1353 (m), 1205 (m), 1150 (m) cm^{-1}; MS m/z 280 (M^+) 209, 170, 153, 135, 109; HRMS calcd for $C_{10}H_{17}IO$ 280.0325, found 280.0328; Anal. Calcd for $C_{10}H_{17}IO$: C, 42.87; H,6.11. Found: C, 42.92; H, 6.13.
5. The aldol reaction of allenoates with benzaldehyde has been shown in the literature: Taniguchi, M.; Hino, T.; Kishi, Y. *Tetrahedron Lett.* **1986**, *27*, 4767.
6. Spectroscopically detectable TMS-allenoate has been reported in the literature: Taniguchi, M; Kobayashi, S.; Nakagawa, M.; Hino, T.; Kishi, Y. *Tetrahedron Lett.* **1986**, *27*, 4763.

(*Received in Japan* 3 *April* 1993; *accepted* 6 *January* 1994)