ORGANIC LETTERS

2003
Vol. 5, No. 9
1547−1550

Highly Stereoselective Synthesis of Novel α-Haloenamides via a Mild and Efficient Hydrohalogenation of Ynamides

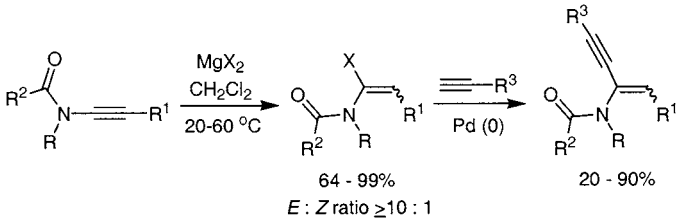
Jason A. Mulder, Kimberly C. M. Kurtz, Richard P. Hsung,*,† Heather Coverdale, Michael O. Frederick,‡ Lichun Shen, and Craig A. Zificsak

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

hsung@chem.umn.edu

Received February 24, 2003

ABSTRACT



A highly stereoselective preparation of novel chiral (*E*)-α-haloenamides under mild conditions utilizing magnesium halide salts is described. This unexpected mild and efficient hydrohalogenation reaction highlights another synthetic utility of ynamides.

The evidence for a renewed interest in ynamide chemistry has been compelling in recent years.[1−14] Ynamides have become proven equivalents of classical ynamines[10] because they possess the right balance between reactivity and stability, allowing them to be handled easily and utilized in a diverse array of highly stereoselective inter- and intramolecular reactions;[3−7] this versatility would be nearly impossible to

† Recipient of a 2001 Camille Dreyfus Teacher-Scholar Award.

‡ Recipient of a 2002 Pfizer Undergraduate Summer Fellowship.

(1) For a recent review on ynamides and ynamines, see: Zificsak, C. A.; Mulder, J. A.; Hsung, R. P.; Rameshkumar, C.; Wei, L.-L. *Tetrahedron* **2001**, *57*, 7575.

(2) For ealier work, see: (a) Janousek, Z.; Collard, J.; Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 917. (b) Goffin, E.; Legrand, Y.; Viehe, H. G. *J. Chem. Res., Synop.* **1977**, 105. (c) Mahamoud, A.; Galy, J. P.; Vincent, E. J.; Barbe, J. *Synthesis* **1981**, 917. (d) Balsamo, A.; Macchia, B.; Macchia, F.; Rossello, A.; Domiano, P. *Tetrahedron Lett.* **1985**, *26*, 4141. (e) Tikhomirov, D. A.; Eremeev, A. V. *Chem. Heterocycl. Compd.* **1987**, *23*, 1141.

(3) (a) Tanaka, R.; Hirano, S.; Urabe, H.; Sato, F. *Org. Lett.* **2003**, *5*, 67. (b) Saito, N.; Sato, Y.; Mori, M. *Org. Lett.* **2002**, *4*, 803. (c) Hoffmann, R. W.; Brückner, D. *New J. Chem.* **2001**, *25*, 369.

(4) (a) Rainier, J. D.; Imbriglio, J. E. *J. Org. Chem.* **2000**, *65*, 7272. (b) Rainier, J. D.; Imbriglio, J. E. *Org. Lett.* **1999**, *1*, 2037.

(5) (a) Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3281. (b) Witulski, B.; Gössmann, M. *Synlett* **2000**, 1793. (c) Witulski, B.; Buschmann, N.; Bergsträsser, U. *Tetrahedron* **2000**, *56*, 8473. (d) Witulski, B.; Stengel, T.; Fernàndez-Hernàndez, J. M. *Chem. Commun.* **2000**, 1965. (e) Witulski, B.; Gössmann, M. *Chem. Commun.* **1999**, 1879. (f) Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 489. (g) Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed.* **1998**, *38*, 2426.

(6) (a) Minière, S.; Cintrat, J.-C. *J. Org. Chem.* **2001**, *66*, 7385. (b) Minière, S.; Cintrat, J.-C. *Synthesis* **2001**, 705. (c) Timbart, L.; Cintrat, J.-C. *Chem. Eur. J.* **2002**, *8*, 1637.

(7) Schottelius, M. J.; Chen, P. *Helv. Chim. Acta* **1998**, *81*, 2341.

(8) (a) Brückner, D. *Synlett* **2000**, 1402. (b) Fromont, C.; Masson, S. *Tetrahedron* **1999**, *55*, 5405. (c) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, *61*, 5440

(9) (a) Majumdar, K. C.; Ghosh, S. K. *Synth. Commun.* **1994**, *24*, 217. (b) Joshi, R. V.; Xu, Z.-Q.; Ksebati, M. B.; Kessel, D.; Corbett, T. H.; Drach, J. C.; Zemlicka, J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1089. (c) Radl, S.; Kovarova, L. *Collect. Czech. Chem. Commun.* **1991**, *56*, 2413. (d) Novikov, M. S.; Khlebnikov, A. F.; Kostikov, R. R. *J. Org. Chem. USSR* **1991**, *27*, 1576

(10) For reviews on ynamines, see: (a) Himbert, G. In *Methoden Der Organischen Chemie* (*Houben-Weyl*); Kropf, H., Schaumann, E., Eds.; Georg Thieme Verlag: Stuttgart, 1993; pp 3267−3443. (b) Collard-Motte, J.; Janousek, Z. *Top. Curr. Chem.* **1986**, *130*, 89. (c) Ficini, J. *Tetrahedron* **1976**, *32*, 1448.

(11) (a) Huang, J.; Xiong, H.; Hsung, R. P.; Rameshkumar, C.; Mulder, J. A.; Grebe, T. P. *Org. Lett.* **2002**, *4*, 2417. (b) Mulder, J. A.; Hsung, R. P.; Frederick, M. O.; Tracey, M. R.; Zificsak, C. A. *Org. Lett.* **2002**, *4*, 1383. (c) Hsung, R. P.; Zificsak, C. A.; Wei, L.-L.; Douglas, C. J.; Xiong, H.; Mulder, J. A. *Org. Lett.* **1999**, *1*, 1237.

(12) Frederick, M. O.; Mulder, J. A.; Tracey, M. R.; Hsung, R. P.; Huang, J.; Kurtz, K. C. M.; Shen, L.; Douglas, C. *J. Am. Chem. Soc.* **2003**, *125*, 2368.

(13) For our original synthesis, see: Wei, L.-L.; Mulder, J. A.; Xiong, H.; Zificsak, C. A.; Douglas, C. J.; Hsung, R. P. *Tetrahedron* **2001**, *57*, 459.

10.1021/ol0300266 CCC: $25.00
Published on Web 04/05/2003

achieve using traditional ynamines. In our own studies, we have explored tandem en-ynamide RCM, stereoselective Ficini−Claisen rearrangements, and other pericyclic cycloadditions.[11] We have also recently reported an improved ynamide synthesis involving a copper-catalyzed coupling of amides and alkynyl bromides[12] that should improve the accessibility of ynamides,[13,14] thereby allowing greater synthetic utility. With these accomplishments in hand, we further explored new cycloaddition reactions of ynamides. Instead we unexpectedly discovered a mild, facile, and highly stereoselective preparation of (*E*)-α-haloenamides (Figure 1).

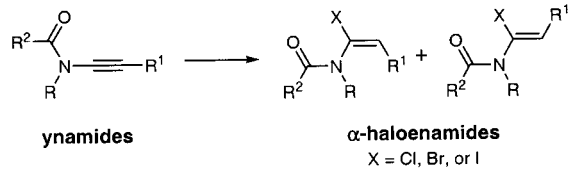
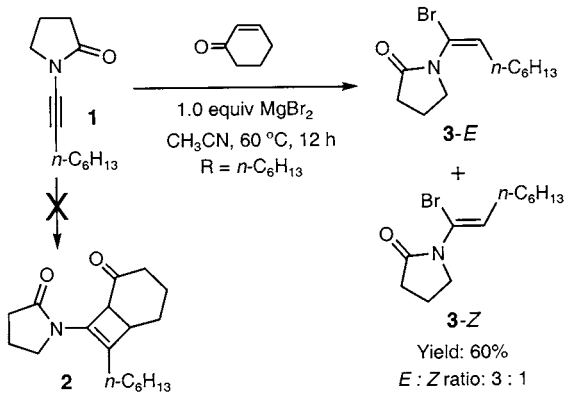


Figure 1.

α-Haloenamides are a synthetically versatile variant of enamides.[15−17] α-Haloenamides offer rapid access to α-metalated enamides that can serve as α-acyl anion equivalents[18] or be involved transition metal mediated reactions.[6a,c] Despite this versatility, there are a very few practical preparations of α-haloenamides, thereby severely limiting their synthetic utility. One of the more useful existing protocols involves direct addition of hydrogen halide (HX) across the alkyne.[19] However, this method often results in poor regio- and stereochemical control, and separation of the resulting isomeric products is often nontrivial. Hydrohalogenation is also a common method for preparation of other α-halo-heteroatom-substituted alkenes,[20,21] albeit with few known chiral examples.[20a,d] One recent improvement to this protocol is Jin's highly selective and elegant synthesis of α-halo vinyl ethers[20a−c] and sulfides[20d] using HX generated in situ from TMSX and methanol. We report here a highly stereoselective preparation of chiral α-haloenamides via a mild and unexpected hydrohalogenation of ynamides.

In an attempt to utilize Lewis acids to facilitate the [2 + 2] cycloaddition[22,23] of ynamide **1** with cyclohexenone (shown in Scheme 1) $MgBr_2$ (1.0 equiv) was added to the

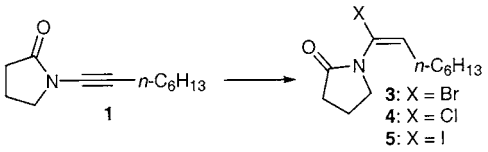
Scheme 1



reaction mixture. The reaction did not yield any of the desired cycloadducts **2** but instead provided the α-haloenamides **3**[24] in 60% yield with a modest *E*/*Z* ratio of 3:1[25] via an unexpected hydrohalogenation of ynamide **1**. The regioselectivity was very high with no (*E*)- or (*Z*)-*β*-haloenamide found.

We investigated the reaction variables of our α-haloenamide synthesis as summarized in Table 1. The hydrohalogenation reaction can be carried out in a variety of solvents as seen utilizing ynamide **1** (entries 1−4), with only the use of methanol giving undesired products (entry 1). With CH_3CN and THF, reactions gave reasonable yields of α-halo-

Table 1.



entry	metal halide	pdt	solvent	temp (°C)	time (h)	isolated yield (%)	E:Z[a]
1	$MgBr_2$	**3**	MeOH	65	48	0	na
2	$MgBr_2$	**3**	CH_3CN	65	8	72	87:13
3	$MgBr_2$	**3**	THF	65	48	70	89:11
4	$MgBr_2$	**3**	$(CH_2Cl)_2$	25	24	85	≥96:4
5	$MgCl_2$	**4**	CH_3CN	65	24	71	95:5
6	$MgCl_2$	**4**	$(CH_2Cl)_2$	100	24	75	95:5
7	MgI_2	**5**	CH_3CN	65	24	80	40:60
8	MgI_2	**5**	$(CH_2Cl)_2$	25	3	90	≥96:4
9	CuI	**5**	CH_3CN	25	24	0	na
10	$ZnCl_2$	**5**	CH_3CN	25	24	0	na
11	NaBr	**3**	CH_3CN	65	24	0	na

[a] Ratio determined by ^1H and/or ^{13}C NMR.

(14) For a review on synthesis of ynamides, see: Mulder, J. A.; Kurtz, K. C. M.; Hsung, R. P. *Synlett* **2003**, in press.

(15) For reviews on enamides, see: (a) Rappoport, Z. The chemistry of enamines. In *The Chemistry of Functional Groups*; John Wiley and Sons: 1994, New York. (b) Whitesell, J. K.; Whitesell, M. A. *Synthesis* **1983**, 517. (c) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975. (d) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 3363. (e) Lenz, G. R. *Synthesis* **1978**, 489.

(16) For recent studies involving enamides, see: a) Fuchs, J. R.; Funk, R. L. *Organic Lett.* **2001**, *3*, 3349. (b) Abbiati, G.; Clerici, F.; Gelmi, M. L.; Gambini, A.; Pilati, T. *J. Org. Chem.* **2001**, *66*, 6299. (c) Maeng, J.-H.; Funk, R. L. *Org. Lett.* **2000**, *3*, 1125. (d) Shen, R.; Porco, Jr., J. A. *Org. Lett.* **2000**, *2*, 1333. (e) Bach, T.; Schröder, J.; Brandl, T.; Hecht, J.; Harms, K. *Tetrahedron* **1998**, *54*, 4507. (f) Ogawa, T.; Kiji, T.; Hayami, K.; Suzuki, H. *Chem. Lett.* **1991**, 1443.

(17) For recent examples of α-haloenamides (excluding heterocyclic variants), see: (a) Boiko, V. I.; Sinitsa, A. A.; Onys'ko, P. P. *Russ. J. Gen. Chem.* **1999**, *69*, 1879. (b) Meier, S.; Werthwein, E. U. *Chem. Ber.* **1990**, *123*, 2339. (c) Kondrat'eva, G. Y.; Agafonov, N. E.; Stashina, G. A. *Izv. Akad. Nauk, Ser. Khim.* **1989**, *9*, 2038. (d) Ivanov, C.; Dobrev, A.; Nechev, L.; Nikiforov, T. *Synth. Commun.* **1989**, *19*, 297. (e) Mironova, D. F.; Loginova, N. A. *Ukr. Khim. Zh.* **1986**, *52*, 71. (f) Del'tsova, D. P.; Zeifman, Y. V.; Gambaryan, N. P. *Izv. Akad. Nauk, Ser. Khim.* **1985**, *11*, 2533. (g) Bal'on, Y. G.; Moskaleva, R. N. *Zh. Org. Khim.* **1983**, *19*, 2456.

(18) Lander, P.; Hegedus, L. S. *J. Am. Chem. Soc.* **1994**, *116*, 8126.

(19) (a) Bal'on, Y. G.; Moskaleva, R. N. *Zh. Org. Khim.* **1983**, *19*, 2456. (b) Bal'on, Y. G.; Moskaleva, R. N. *Zh. Org. Khim.* **1978**, *14*, 147.

enamide **3** but required reaction temperatures of 60 °C or higher to drive the reaction to completion (entries 2 and 3).

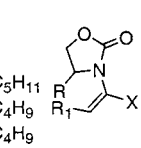
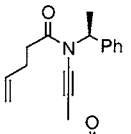
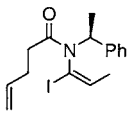
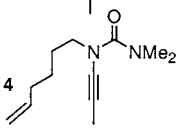
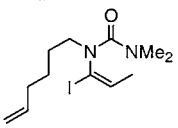
We found CH_2Cl_2 to be an ideal solvent for this reaction (entry 4), allowing the reaction to progress at ambient temperature leading to the (*E*)-haloenamide **3** in high yield with high diastereoselectivity. The use of $MgCl_2 \cdot 6H_2O$ (entries 5 and 6) required elevated reaction temperatures ≥65 °C in a sealed vial to drive the reaction, and thus 1,2-dichloroethane was the preferred solvent (entry 6). Poor solubility of $MgCl_2 \cdot 6H_2O$ may be inhibitive to the reaction in this instance. CH_2Cl_2 was also found to be the solvent of choice for use with MgI_2, especially with respect to stereoselectivity (entry 7 versus 8). In contrast to the reasonable yields obtained using CH_3CN in entries 2, 5, and 7, attempts to use additives other than magnesium halides in CH_3CN failed even at extended reaction times. The use of CuI (entry 9) led to undesired products, $ZnCl_2$ (entry 10) led exclusively to ynamide hydrolyses, and NaBr (entry 11) yielded no reaction.

Equipped with optimized reaction conditions, we probed the scope of this hydrohalogenation reaction using a variety of different ynamides (Table 2). Ynamides of the Evans' auxiliary[26] **6**−**8** (entries 1−3), Sibi auxiliary[27] **9** (entries 4 and 5), and indanol-type **10**−**12** (entries 6, 7, 11−14) were all successfully converted to the respective α-haloenamides **15**−**21** and **24**−**27** in high yield with high levels of regio- and stereochemical control. This methodology is applicable also to acyclic ynamides, such as chiral acyclic ynamide **13** and urea-based ynamide **14**, which form α-haloenamides **28** and **29**, respectively, with excellent selectivity. The modest yield for the urea-based ynamide **14** is due to slow conversion rates with this type of system. Stereochemistry of the (*E*)-α-haloenamide was unambiguously assigned from the X-ray crystal structure of the major isomer of α-haloenamide **26**, thereby suggesting a *syn*-addition of HX.[20a]

It is noteworthy that to compare Jin's preparation of (*E*)-α-halo vinyl ethers we treated ynamide **10** with 1.0 equiv each of trimethylsilyl bromide (TMSBr) and MeOH at −40 °C (entry 8), producing a single isomer of **21** in 62% yield in favor of the (*E*)-isomer along with 10% hydrolyses of **10**. An effort to extend this methodology to form other useful α-substituted enamides using TMSOTf and TMSCN failed even at elevated temperatures (see entries 9 and 10).

The proposed source of HX in this unexpected hydrohalogenation of ynamides is in situ generation of HX from the magnesium salt MgX_2 and trace H_2O in the reaction. The source of the serendipitous water could be the magnesium salt and/or the reaction solvent. To support this proposition, hydrobromination of ynamide **11** was carried out again under the standard conditions (freshly opened CH_2Cl_2 with water concentration 0.01% v/v) along with a second reaction conducted under more vigorously anhydrous conditions: (a) dichloromethane freshly distilled from CaH_2, and (b) anhydrous $MgBr_2$ freshly prepared from magnesium metal and 1,2-dibromoethane. The conversion rate for the two reactions was monitored by LCMS. After 4.5 h, the conversion to product for the standard "wet" reaction was 37% and only 11% for the anhydrous version. After 19 h, the conversions were 71% and 28%, respectively. This rate difference suggests that the anhydrous system inhibited the formation of HBr in situ.

Table 2.

entry	ynamide[a]	R =	R_1 =	product	pro-acid	yld%[b]	*E* : *Z*[c]
1	**6**	*R*-Ph	Ph		MgI_2	84	≥96:4
2	**7**	*R*-CH_2Ph	Ph		MgI_2	86	≥96:4
3	**8**	*S*-*i*Pr	*n*-C_5H_{11}		MgI_2	64	≥96:4
4	**9**	*R*-$CHPh_2$	*n*-C_4H_9		$MgBr_2$	84	≥96:4
5	**9**	*R*-$CHPh_2$	*n*-C_4H_9		MgI_2	82	≥96:4
6	**10**		*n*-C_5H_{11}		MgI_2	90	91:9
7	**10**		*n*-C_5H_{11}		$MgBr_2$	96	≥96:4
8	**10**		*n*-C_5H_{11}		TMSBr	62	≥96:4
9	**11**		Ph		TMSOTf	0	N/A
10	**11**		Ph		TMSCN	0	N/A
11	**11**		Ph		$MgBr_2$	74	≥96:4
12	**11**		Ph		MgI_2	71	≥96:4
13	**12**		*i*Pr		$MgBr_2$	77	94:6
14	**12**		*i*Pr		MgI_2	99	≥96:4
15	**13**				MgI_2	85	≥96:4
16	**14**				MgI_2	37	≥96:4

[a] Reaction conditions: ynamide (0.03 M) and 1 equiv of MgX_2 in wet CH_2Cl_2, 3−18 h, rt. [b] Isolated yield. [c] Ratio determined by ^1H and/or ^{13}C NMR.

(20) Chiral and achiral α-halo vinyl ethers: (a) Yu, W.; Jin, Z. *J. Am. Chem. Soc.* **2000**, *122*, 9840. Applications in synthesis: (b) Yu, Z.; Jin, Z. *J. Am. Chem. Soc.* **2001**, *123*, 3369. (c) Yu, Z.; Jin, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6576. (d) Su, M.; Kang, Y.; Yu, W.; Hua, Z.; Jin, Z. *Org. Lett.* **2002**, *4*, 691. α-Halo vinyl sulfides: Su, M.; Yu, W.; Jin, Z. *Tetrahedron Lett.* **2001**, *42*, 3771.

(21) Other recent examples for α-halo vinyl ethers: (a) Bacilieri, C.; Reic, S.; Neuenschwander, M. *Helv. Chim. Acta* **2000**, *83*, 1182. (b) Glazunova, E. Y.; Lutsenko, S. V.; Efimova, I. V.; Trostyanskaya, I. G.; Kazankova, M. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1969**, *34*, 1104. α-Halo vinyl sulfides: (c) Duncan, D.; Livinghouse, T. *J. Org. Chem.* **2001**, *66*, 5237. (d) Stefani, H. A.; Comasseto, J. V.; Petragnani, N. Braga, A. L.; Menezes, P. H. Gusevskaya, E. V. *Phosporus, Sulfur Silicon Relat. Elem.* **1997**, *126*, 211. α-Halo vinyl sulfates: (e) Paley, R. S.; Dios, A. de; Estroff, L. A.; Lafontine, J. A.; Montero, C. et al. *J. Org. Chem.* **1997**, *62*, 6326. (f) Zhong, P.; Huang, X.; Ping-Guo, M. *Tetrahedron* **2000**, *56*, 8921. α-Halo vinyl phosphonates: (g) Kobayashi, Y.; William, A. D. *Org. Lett.* **2002**, *4*, 4241. (h) Zhang, X.; Burton, D. J. *J. Fluorine Chem.* **2001**, *112*, 47.

(22) For a review on thermal [2 + 2] cycloaddition reactions, see: Baldwin, J. E. *Comprehensive Organic Synthesis*; Trost, B. M. Fleming, I.; Pattenden, G., Eds.; Pergamon Press: New York, 1991, Vol. 5, p 63.

(23) For examples of [2 + 2] cycloaddition reaction of ynamines with enones see: (a) Ficini, J.; Krief, A.; Guingant, A.; Desmaele, D. *Tetrahedron Lett.* **1981**, 725. (b) Ficini, J.; Guingant, A.; d'Angelo, J.; Stork, G. *Tetrahedron Lett.* **1983**, 907.

(24) All new compounds are characterized by ^1H NMR, ^{13}C NMR, FTIR, mass spectroscopy, and $[\alpha]^{23}_D$.

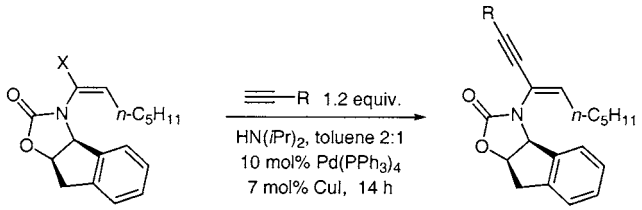
(25) Assigned later by correlating with X-ray structure of α-haloenamide **26**.

(26) (a) Evans, D. A. *Aldrichimica Acta* **1982**, *15*, 23. (b) Heathcock, C. H. *Aldrichimica Acta* **1990**, *23*, 99.

(27) (a) Sibi, M. P.; Deshpande, P. K.; Ji, J. G. *Tetrahedron Lett.* **1995**, *36*, 8965. (b) Sibi, M. P.; Ji, J. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 190. (c) Nakai, T.; Setoi, H.; Kageyama, Y. *Tetrahedron Lett.* **1981**, *22*, 4097.

There are many potential applications for α-haloenamides in organic synthesis. They should provide efficient entry into α-stannyl enamides such as those used by Hegedus[18,28] and Cintrat.[6,29] Our methodology offers the additional benefit of being able to form α-stannyl enamides that possess diverse functionality at the *β*-carbon as well. In addition, α-haloenamides are excellent candidates for use in transition metal mediated reactions such as Sonagashira coupling.[30]

Scheme 2



21 : X = Br	**30** : R = TMS	74%
21	**31** : R = Ph	79%
20 : X = I	**30** : R = TMS	79%
20	**31** : R = Ph	90%
20	**32** : R = CO_2CH_3	20%

As shown in Scheme 2, both α-bromo- and α-iodoenamides **21** and **20** underwent efficient coupling with trimethylsilylacetylene and phenylacetylene to yield enynes **30** and **31** in 74% to 90% yield, respectively. Even electron-poor propiolate will couple with α-iodoenamide **20**, albeit in lower yield. The reaction must be stopped at 50% conversion to actually minimize an ensuing cycloaddition of enyne **32** with propiolate. The enyne products **30**−**32** have a variety of uses in organic chemistry, including being prime candidates for cross-benzannulation[31] or Diels−Alder reactions,[32] with the chiral auxiliary of the enamide potentially providing asymmetric induction.[33]

We have described a highly stereoselective synthesis of (*E*)-α-haloenamides using magnesium salts in wet solvents at ambient or moderate temperature. In conjunction with our one-step ynamide synthesis using Cu(I) salts, this reaction provides a facile entry to α-haloenamides, which are versatile synthons shown to undergo subsequent Sonagashira couplings en route to chiral amide-substituted enynes. This unexpected hydrohalogenation reaction highlights another synthetic utility of ynamides. Further applications of α-haloenamides are currently under investigation.

Acknowledgment. The authors thank the National Science Foundation (CHE-0094005) for support of this work. J.A.M. thanks UMN for a Dissertation Fellowship.

Supporting Information Available: Experimental procedures and characterization data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0300266

(28) Riches, A. G.; Wernersbach, L. A.; Hegedus, L. S. *J. Org. Chem.* **1998**, *63*, 4691.

(29) Minière, S.; Cintrat, J.-C. *Synthesis* **2001**, 705.

(30) Sonagashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(31) For an example, see: Saito, S.; Uchiyama, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 4338.

(32) Examples of enynes in Diels Alder reactions: (a) Hoffmann, H. M. R.; Mucha, B.; Oehlerking, H. H.; Prahst, G. W. *Tetrahedron* **1993**, *49*, 8999. (b) Spino, C.; Crawford, J. *Tetrahedron Lett.* **1994**, *35*, 5559. (c) Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218.

(33) Xiong, H.; Hsung, R. P.; Shen, L.; Hahn, J. M. *Tetrahedron Lett.* **2002**, *43*, 4449.