Pergamon

Tetrahedron Letters, Vol. 38, No. 25, pp. 4525-4526, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00920-9

Stereoselective Synthesis of either *E*- or *Z*-Diiodoalkenes from Alkynes using ICl and Iodide.

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Abstract: Reaction of alkynes with ICl and an iodide source results in the stereoselective formation of diiodoalkenes in moderate to high yield. At r.t., the reaction is stereospecific, resulting in the formation of *E*-diiodoalkenes, however lowering the temperature and using a more soluble iodide source results in a stereoselective formation of the Z-diiodoalkenes. © 1997 Elsevier Science Ltd.

Diiodoalkenes are useful intermediates in direct coupling reactions for forming new carbon-carbon bonds, either involving organo-lithium[1], organo-copper[2], or palladium catalysed cross-coupling reactions[3]. Following recent work on the stereoselective synthesis of styrenes and polyenes using a combination of Heck and Suzuki coupling processes[4], a stereoselective synthesis of mono-iodoalkenes *via* iodo-deboronation of alkenyl boronates mediated by ICl[5] was developed. More recently a stereoselective synthesis of diiodoalkenes was required, for which several procedures have been reported in the literature which generally involve the reaction of iodine and related reagents with alkynes,[6] or from organometallic compounds[7]. In this communication we report a stereospecific and efficient synthesis of *E*-diiodoalkenes and stereoselctive formation of Z-diiodoalkenes, from the reaction of alkynes with ICl and iodide ion (**Equation 1** and **Table 1**).

Equation 1.

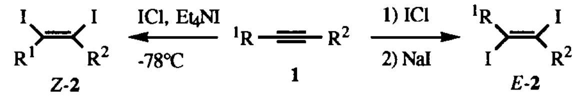

Table 1.

Entry	Acetylene 1	Method[a]	Temp. / °C	Solvent	Time / h	*E*:*Z* ratio[b] of **2**	Isolated yield of **2**[c,d,e] / %
1	$\equiv$— CH_2OAc	A	0 - rt	CH_2Cl_2	4	100 : 0	75
2	$\equiv$— Ph	A	"	"	6	100 : 0	86
3	$\equiv$— Ph	B	-78	"	1	0 : 100	70
4	$\equiv$— n-Pr	A	0 - rt	THF	12	100 : 0	65
5	$\equiv$— n-Pr	B[f]	-78	CH_2Cl_2		18 : 82	42
6	$\equiv$— n-C_5H_{11}	A	0 - rt	"	14	100 : 0	69
7	$\equiv$— n-C_5H_{11}	B	-78	"	0.25	20 : 80	65
8	Et—$\equiv$— Et	A	0 - rt	"	14	100 : 0	56
9	$\equiv$— CH_2CH_2OBn	A	"	"	6	100 : 0	25
10	$\equiv$— CH_2CH_2OBn	B	-78	"	1	40 : 60	40
11	$\equiv$— CH_2OPh	A	0 - rt	"	14	100 : 0	75
12	$\equiv$— CO_2Me	A	"	"	4	100 : 0	84

[a]See ref. 8. [b]Isomeric ratios were determined by both ^1H and ^{13}C n.m.r. [c]All crude yields were *ca.* quantitative and isolated yields were after silica gel chromatography. [d]All known compounds were identical to those reported in the literature (see refs. 6). [e]New compounds had satisfactory spectroscopic and analytical properties which agreed with the assigned structures, see ref. 9. [f]NaI was used in place of Et_4NI.

Alkynes **1** react with ICl and sodium iodide at 0°C to room temperature (**Method A**) to stereospecifically provide the thermodynamic *E*-diiodoalkenes **2** in essentially quantitative crude yields (**Equation 1**). Purification by silica gel chromatography gave the pure *E*-alkenes **2** in medium to high yields (**Table 1**). In order to try and derive the corresponding *Z*-alkenes, various reaction conditions were investigated which resulted in the discovery that lower temperature conditions were necessary to achieve stereoselectivity and that treatment of the alkyne **1** with ICl had to precede treament with the iodide source (**Method B**). However, even under these conditions, variable stereocontrol was observed (**Table 1**). Thus, for phenylacetylene (Entry 3), the reaction was stereospecific giving the pure *Z*-diiodide in 70 % yield. For 1-pentyne and 1-heptyne (Entries 5 and 7 respectively), stereocontrol was approximately 4:1 (*Z*:*E*), however benzyloxybutyne (entry 10) produced a 60:40 mixture of *Z* and *E*-diiodides **2** after one hour (longer reaction times caused slow conversion to the *E*-diiodide). The mechanism for the diiodination reactions is likely to be very similar to that discussed by Barluenga[6d].

Further applications of this work will be reported in due course.

Acknowledgements.

We thank the S.E.R.C. for an Earmarked Studentship (to S.S.) and for a consumables grant (ref. GR/H27724).

References and Notes.

1. Barluenga, J.; Montserrat, J.M.; and Flórez, J.; *J. Org. Chem.*, **1993**, *58*, 5976-5980.
2. Staab, H.A.; and Shin, H.J.; *Chem. Ber.*, **1977**, *110*, 631-637.
3. a) Huynh, C.; and Linstrumelle, G.; *Tetrahedron*, **1988**, *44*, 6337-6344; b) Wright, M.E.; and Lowe-Ma, C.K.; *Organometallics*, **1990**, *9*, 347-352.
4. a) Hunt, A.R.; Stewart, S.K.; and Whiting, A.; *Tetrahedron Lett.*, **1993**, *34*, 3599-3602; b) Stewart, S.K. and Whiting, A.; *J. Organomet. Chem.*, **1994**, *482*, 293-300; c) *Idem*; *Tetrahedron Lett.*, **1995**, *36*, 3925-3928.
5. *Idem*; *ibid*, **1995**, *36*, 3929-3932.
6. a) Hollins, R.A.; and Campos, M.P.A.; *J. Org. Chem.*, **1979**, *44*, 3931-3934; b) Spraul, M.; and Griesbaum, K.; *Chem Ber.*, **1983**, *116*, 2641-2652; c) Hondrogiannis, G.; Lee, L.C.; Kabalka, G.W.; and Pagni, R.M.; *Tetrahedron Lett.*, **1989**, *30*, 2069-2070; d) Doad, G.J.S.; Austin, D.J.; and Owen, T.C.; *J. Chem. Research (S)*, **1989**, 313; e) Barluenga, J.; Rodríguez, M.A.; and Campos, P.J.; *J. Org. Chem.*, **1990**, *55*, 3104-3106.
7. a) Victor, R.; *J. Organomet. Chem.*, **1977**, *127*, C25-C28; b) Beaudet, I.; Parrain, J.-L.; and Quintard, J.-P.; *Tetrahedron Lett.*, **1991**, *32*, 6333-6336; c) Marek, I.; Alexakis, A.; and Normant, J.-F.; *ibid*, **1991**, *32*, 6337-6340.
8. General procedures. **Method A**: The alkyne (1.5mmol) was added to a solution of ICl (1.65 mmol) in either CH_2Cl_2 or THF (15ml) under Ar at 0 °C (see **Table 1**), followed by NaI (6.0mmol). The mixture was allowed to warm to r.t., stirred for the time shown in **Table 1** and filtered through Celite. Residual iodine was removed by brief washing with 10% aq. sodium metabisulfite. The organic extract was washed with aq. sodium chloride, dried ($MgSO_4$) and evaporated to give the crude diodide. Purification was achieved by SiO_2 chromatography to give the pure diiodides[9]. **Method B**: As **Method A**, except that Et_4NI was used in place of NaI and reactions were carried out at -78°C.
9. Selected data for diiodides in **Table 1**: Entry 3, *Z*-**2** (R^1 = H, R^2 = Ph), δ^1H [6.7(1H, s), 7.3-7.5(5H, m)], $\delta^{13}C$ [73.0, 102.9, 128.3, 128.5, 129.0, 137.7]; Entry 9, *E*-**2** (R^1 = H, R^2 = CH_2CH_2OBn) δ^1H [3.0(2H, t, J7.1), 3.7(2H, t, J7.1), 4.6(2H, s), 7.0(1H, s), 7.4-7.6(5H, m)], $\delta^{13}C$[44.8, 67.6, 72.9, 81.2, 127.5, 128.2, 128.6, 140.1]; Entry 10 *Z*-**2** (R = CH_2CH_2OBn) δ^1H[3.0(2H, t, J6.5), 3.6(2H, t, J6.5), 4.4(2H,s), 6.3(1H, s), 7.2-7.4(5H, m)], $\delta^{13}C$[39.1, 66.5, 72.9, 99.1, 128.3, 128.4, 128.6, 138.0].

(*Received in UK* 29 *April* 1997; *accepted* 9 *May* 1997)