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DIASTEREOSELECTIVE SYNTHESIS OF (E)-1-TRIMETHYLSILYL-3-EN-1-YNES BY PALLADIUM-CATALYZED CROSS-COUPLING REACTION BETWEEN TRIMETHYLSILYLETHYNYLZINC CHLORIDE AND STEREOISOMERIC MIXTURES OF 1-BROMO-1-ALKENES[1]

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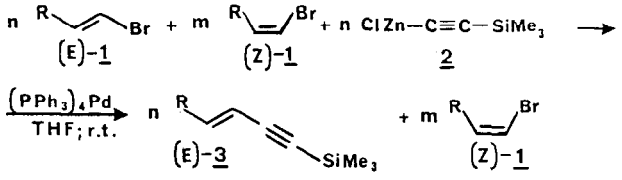
Summary: In the stereospecific palladium-catalyzed cross-coupling reaction of trimethylsilylethynylzinc chloride, (E)-1-bromo-1-alkenes react preferentially in the presence of the corresponding (Z)-stereoisomers.

In continuation of our studies on highly diastereoselective palladium-catalyzed reactions involving the use of diastereoisomeric mixtures of alkenyl bromides[2-4], we now wish to report a simple and convenient procedure for the diastereoselective synthesis of (E)-1-trimethylsilyl-3-en-1-ynes (3). This procedure stems from the observation that in the stereospecific palladium-catalyzed reaction of trimethylsilylethynylzinc chloride (2), (E)-1-bromo-1-alkenes,(E)(1), react preferentially in the presence of the corresponding (Z)-stereoisomers,(Z)(1).

Thus, when treated with n equiv of 2 and 2 mol% of $(PPh_3)_4Pd$ in THF at room temperature for 8h, an easily available diastereoisomeric mixture of 1 which contains n equiv of (E)-1 affords in good isolated yields an (E)-1-trimethylsilyl-3-en-1-yne (3) having 95.5-98.4% stereoisomeric purity[5,6].



Some typical results are summarized in Table.

TABLE

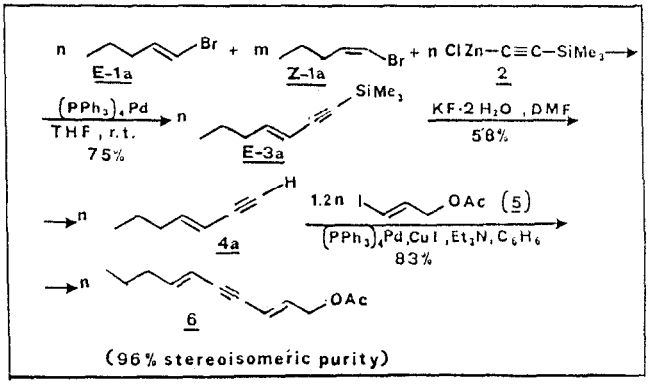
Diastereoselective synthesis of (E)-1-trimethylsilyl-3-en-1-ynes (3).

Reagent		Product : (E)-3		
R	(E)/(Z)-1	Isolated yield(%)[a]	Stereoisomeric purity(%)	Compound
n-C_3H_7	54.1/45.9	75.0	95.5	3a
n-C_4H_9	38.0/62.0	77.0	98.4	3b
n-C_5H_{11}	61.4/38.6	80.9	⩾96.0	3c

a) Based on (E)-1

It is interesting to note that compounds 3 can be easily transformed into the corresponding (E)-3-en-1-ynes (4)[7,8], some of which are interesting intermediates for the synthesis of naturally occurring polyunsaturated compounds. Thus, when treated with a slurry of KF $2H_2O$ in DMF at 25°, compound 3a produces the corresponding (E)-3-en-1-yne, 4a, in 58% yield. The reaction of 4a with stereoisomerically pure (E)-1-acetoxy-3-iodo-1-propene (5) (1.2 eq), in the presence of $(PPh_3)_4Pd$ (0.03 eq), CuI (0.06 eq) and Et_3N (3 eq) in benzene at 20° for 24h, affords 96% stereoisomerically pure (2E,6E)-1-acetoxy-2,6-decadien-4-yne (6) in 83% isolated yield (Scheme 1). Compound 6 is an acetylenic substance isolated from Grindelia species[9].

SCHEME 1



Obviously, similar procedures could be employed to prepare other naturally-occurring acetylenic compounds characterized by an (E,E)-1,5-dien-3-yne moiety[9,10].

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REFERENCES AND NOTES

1) This work was presented as a part of R.R.'s lecture at the II Session of the Ischia Advanced School of Organic Chemistry (Ischia, May 25-30, 1986); 2) R.Rossi, A.Carpita, and P.Piccardi, in "Pesticide Chemistry: Human Welfare and the Environment", J.Miyamoto and P.C.Kearney Eds, Pergamon Press, Vol 1, pp 129-134 (1983); 3) R.Rossi and A.Carpita, Tetrahedron Lett., 27, 2529 (1986); 4) A.Carpita and R.Rossi, Tetrahedron Lett., in the press; 5) The stereoisomeric purity of the reaction products was evaluated by GLC on a Permaphase PEG capillary column. Their stereochemistry was confirmed by comparing them with stereoisomeric mixtures of (E)- and (Z)-3 prepared by treatment of (E)/(Z)-1 with a large molar excess of 2; 6) All new compounds exhibited satisfactory spectral and physical properties; 7) J.A.Miller and G.Zweifel, Synthesis, 128 (1983); 8) These compounds can be also conveniently prepared by a stereospecific coupling reaction of (E)-1-iodo-1-alkenes with 2-methyl-3-butyn-2-ol, in the presence of catalytic amounts of CuI and $(PPh_3)_4Pd$, using aq 5.5N NaOH as base, C_6H_6 as solvent, and $BnEt_3N^+Cl^-$ as phase transfer agent, followed by treatment of the so obtained enynols with a catalytic amount of solid NaOH in toluene at 110° for 0.5h. This procedure has been employed to prepare (E)-3-nonen-1-yne (4b) in 69.4% overall yield. (For previous examples of Pd-Cu catalyzed reactions between 1-alkynes and alkenyl or aryl halides under phase-transfer conditions see: A.Carpita, A.Lezzi, R.Rossi, F.Marchetti, and S.Merlino, Tetrahedron, 41, 621 (1985) and references cited therein); 9) F.Bohlmann, W.Thefeld, and C.Zdero, Chem.Ber., 103, 2245 (1970); 10) F.Bohlmann and H.C. Hummel, Chem.Ber., 103, 3419 (1970).

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