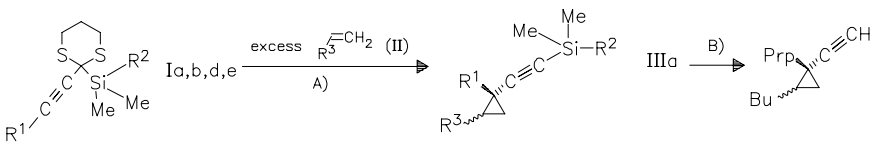
Organo-silicon compounds

S 0060

43- 190

Cyclopropanation and Carbonyl Olefination Utilizing 2-(Alk-1-yn-1-yl)-2-(trialkylsilyl)-1,3-dithianes via Regioselective Generation of Titanium Alkynylcarbene Complexes. — Silylated alkynyl thioacetals are found to react with terminal olefins and carbonyl compounds in a highly regioselective manner to afford cyclopropanes of type (III) or conjugated enynes such as (VII) and (XI). Subsequent desilylation provides a convenient route to functionalized terminal alkynes which are useful synthons. — (TAKEDA*, T.; OZAKI, M.; KUROI, S.; TSUBOUCHI, A.; J. Org. Chem. 70 (2005) 11, 4233-4239; Dep. Appl. Chem., Fac. Technol., Tokyo Univ. Agric. Technol., Koganei, Tokyo 184, Japan; Eng.) — Jannicke

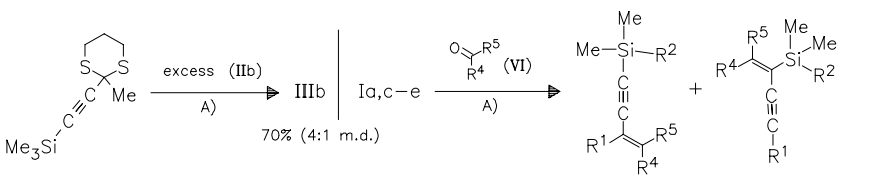


a R^1: —Prp ; R^2: —Me
b R^1, R^2: —Me
c R^1: —Me ; R^2: —tBu
d R^1: —Bu ; R^2: —tBu
e R^1: —Prp ; R^2: —tBu

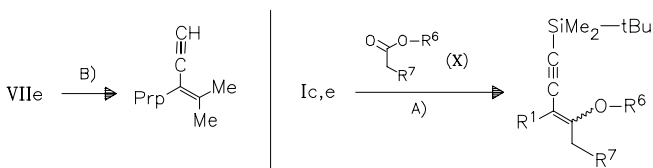
a R^1: —Prp ; R^2: —Me ; R^3: —Bu 67% (~3:2 m.d.)
b R^1, R^2: —Me ; R^3: $—(CH_2)_2—Ph$ 63% (4:1 m.d.)
d R^1: —Bu ; R^2: —tBu ; R^3: —Ph 70% (>30:1 m.d.)
e R^1: —Prp ; R^2: —tBu ; R^3: —Ph 75% (>30:1 m.d.)

92% (~3:2 m.d.)

Prp: $—(CH_2)_3—Ph$ A): excess $Ti(Cp)_2(P(O—Et)_3)_2$, THF, 25°C B): Bu_4NF, THF, 0°C



a R^1: —Prp ; R^2: —Me ; R^4, R^5: —Et 75% (80:20)
c R^1: —Me ; R^2: —tBu ; R^4, R^5: $—(CH_2)_2—Ph$ 71% (100:0)
d R^1: —Bu ; R^2: —tBu ; $R^4—R^5$: —tBu 69% (100:0)
e R^1: —Prp ; R^2: —tBu ; R^4, R^5: —Me 68% (100:0)



c R^1: —Me ; R^6: —Et ; R^7: $—CH_2—Ph$ 68%
e R^1: —Prp ; $R^6—R^7$: 71%