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Ruthenium Catalyzed Dimerization of Trimethysilylacetylene to 1,4-Bis(trimethylsilyl)butatriene and Its Isomerization to (*Z*)-1,4-Bis(trimethylsilyl)-1-buten-3-yne

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Synopsis. Trimethylsilylacetylene was catalytically dimerized by Ru(cod)(cot)/PR_3(cod = 1,5-cyclooctadiene, cot=cyclooctatriene) to give either $Me_3SiCH=C=C=CHSiMe_3$ when $PR_3=PPh_3$ or (*Z*)- $Me_3SiCH=CH-C\equiv CSiMe_3$ when $PR_3=PBu^n_3$, the latter being formed by stereoselective isomerization of initially formed (*Z*)-$Me_3SiCH=C=C=CHSiMe_3$.

Dimerization of terminal acetylenes is a convenient route to an unsaturated C4-skeleton. While transition metal-catalyzed dimerization of terminal acetylenes has been known to give isomers of conjugated enynes generally,[1)] we recently reported in detail a unique dimerization of *t*-butylacetylene to (*Z*)-1,4-di-*t*-butylbutatriene catalyzed by ruthenium complexes.[2)] Since the butatriene framework is calculated to be at a ca. 20 kcal mol^{-1} higher energy level than corresponding enynes (Ref. 2 and Fig. 1) it is expected to be reactive enough and has potential utility in organic synthesis as do conjugated enynes. However, the *t*-butyl substituent used in our previous catalytic reaction is apparently not attractive from the viewpoint of organic synthesis. Although the parent butatriene $H_2C=C=C=CH_2$ may be more useful, it is known to be very unstable and difficult to store.[3)] We therefore aimed to prepare 1,4-bis(trimethylsilyl)butatriene through our reacion, which is expected to have utility in organic synthesis as a substitute for the parent butatriene. During the course of our study to dimerize trimethylsilylacetylene to butatriene, we found the rearrangement described in the title, which provides a simple and practical means for the preparation of (*Z*)-1,4-bis(trimethylsilyl)-1-buten-3-yne selectively. We also report the best reaction conditions to get the originally-intended 1,2,3-butatriene having a trimethylsilyl group at each end.

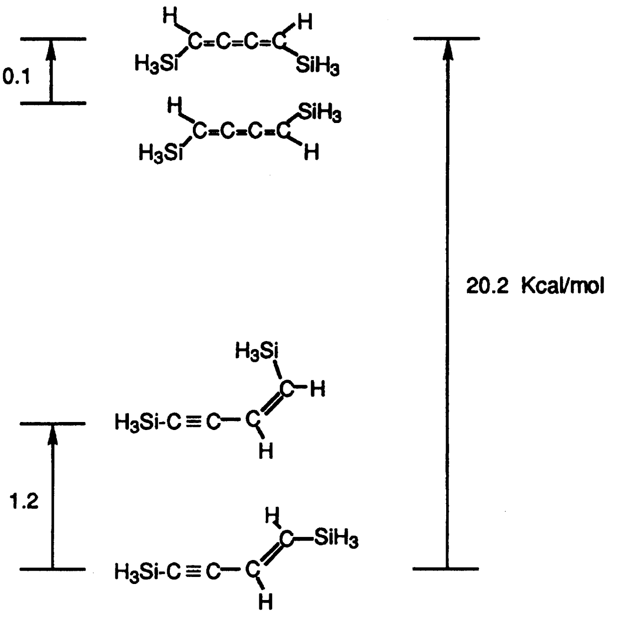
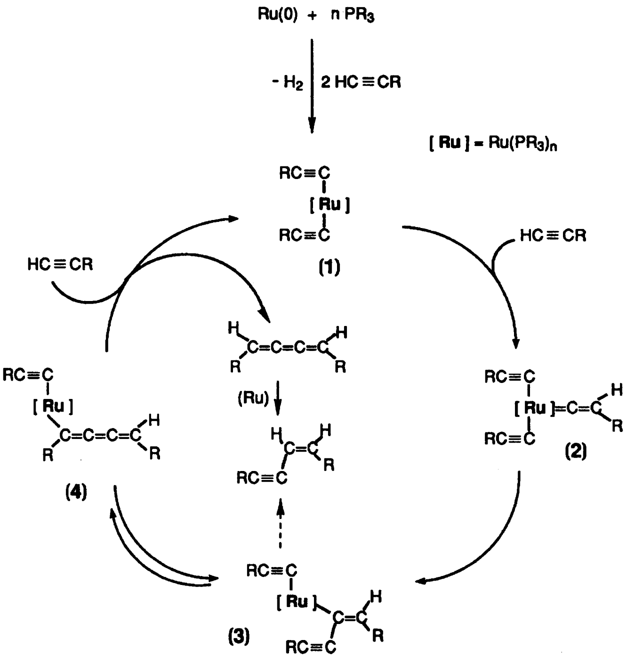


Fig. 1. Relative energies of the isomers. Geometries and energies were calculated by ab initio MO, restricted Hartree–Fock level with Dunning–Huzinaga's full double-zeta basis set.[7)]

Results and Discussion

The activity and selectivity of ruthenium-catalyzed dimerization of $HC\equiv CR$ have been found to be very dependent on the substituent R. $Ru(CO)H_2(PPh_3)_3$ which is one of the most active catalysts for the dimerization of $HC\equiv CBu^t$ is not active for the selective dimerization of $HC\equiv CSiMe_3$. But when a benzene solution of $HC\equiv CSiMe_3$ and a catalytic amount of Ru(cod)(cot)/$P(Bu^n)_3$ (1/3 ratio, cod = 1,5-cyclooctadiene, cot = cyclooctatriene) was simply allowed to stand three days at room temperature under an atmosphere of argon and then fractionally distilled, pure (*Z*)-$Me_3SiCH=CHC\equiv CSiMe_3$ was obtained in an 87% yield. No *E*-isomer was detected. The *E*-isomer has been selectively formed via $RhCl(PPh_3)_3$-catalyzed dimerization as reported by Ishikawa et al.,[4)] most likely via a conventional reaction path, i.e. oxidative addition of HC≡, cis-insertion of the second acetylene into Rh-H, and then coupling of the vinyl alkynyl group.[4,5)]

Scheme 1 illustrates the catalytic cycle which we have previously elucidated for the dimerization of $HC\equiv C^tBu$ to butatriene by the ruthenium catalytic system.[2)] The formation of (*Z*)-enyne reported in the present paper appeared to be resonably interpreted by the same scheme, but with release of the product from intermediate (**3**) by accepting hydrogen from $HC\equiv CSiMe_3$ and regenerating intermediate (**1**). The same dimerization has been communicated recently by Bianchini and co-workers using a tetrapod phosphine complex $[RuP(CH_2CH_2PPh_2)_3(C\equiv CSiMe_3)]^+$ as catalyst and this reaction route has indeed been suggested.[6)] Unexpectedly, detailed investigation of the time-conversion of our reaction clearly showed that a different route was operating: the initial product of the catalytic dimerization was the butatriene and it gradually isomerized to (*Z*)-



Scheme 1.

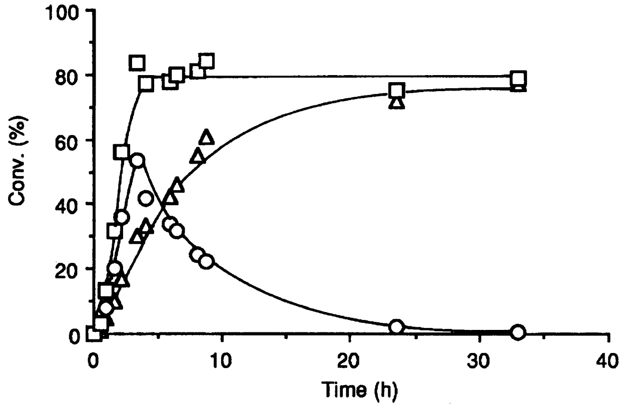


Fig. 2. Time vs. Conversion curve for the dimerizaton of trimethylsilylacetylene by Ru(cod)(cot)/PBu$^n_3$. ○: Me$_3$SiCH=C=C=CHSiMe$_3$. △: (*Z*)-Me$_3$SiCH=CH–C≡CSiMe$_3$. □: Total dimer.

enyne (Fig. 2). The GC analysis showed that the butatriene initially formed contained *Z*- and *E*-forms in a ca. 85/15 ratio. The isomerization of the (*E*)-butatriene to the (*Z*)-enyne was much slower than that of the (*Z*)-butatriene and probably proceeded via initial isomerization to the (*Z*)-butatriene. The possibility that a small part of (*Z*)-Me$_3$SiCH=CHC≡CSiMe$_3$ was formed directly from intermediate (**3**) and HC≡SCiMe$_3$ could not be ruled out.

The isomerization of butatriene to enyne was not observed when triarylphosphine was employed. Thus, a hexane solution of HC≡CSiMe$_3$ in the presence of a catalytic amount of Ru(cod)(cot)/PPh$_3$ (1/6 ratio) gave a 92% yield of dimer which consisted of (*Z*)-Me$_3$SiCH=CHC≡CSiMe$_3$ (5%), (*E*)-Me$_3$SiCH=C=C=CHSiMe$_3$ (19%), and (*Z*)-Me$_3$SiCH=C=C=CHSiMe$_3$ (76%). The enyne could be removed by fractional distillation under reduced pressure.

Reactivity of the novel butatriene towards transition metal complexes, as well as the mechanism of hydrogen transfer which lead to the isomerization of the betatriene to enyne, is now under investigation.

Experimental

IR spectra were obtained with a Shimadzu IR-27G spectrometer. NMR spectra were recorded on a JEOL JNMGX-400 or GX-500 spectrometer using SiMe$_4$ (^{1}H and ^{13}C) as an internal standard. Ru(cod)(cot), was prepared according to the literature.[8] All reactions were carried out under an atmosphere of argon. GC analyses were performed on a Hewlett–Packard 5890 with a 30 m×0.32 mm DB1 column using dodecane as an internal standard.

Dimerization of HC≡CSiMe$_3$ to (*Z*)-Me$_3$SiCH=CHC≡CSiMe$_3$. To a solution of Ru(cod)(cot) (593 mg, 1.9 mmol) and P^{n}Bu$_3$ (1.2 g, 5.9 mmol) in benzene (100 ml) was added HC≡CSiMe$_3$ (48 ml, 340 mmol) and the mixture was allowed to stand at room temperature. After three days, the solvent and unreacted acetylene were evaporated at reduced pressure and the residue was fractionally distilled. The dimer distilled out at 53—54°C/3 mmHg (1mmHg=133.322 Pa) in an 87% yield (29 g).

Selected Spectroscopic Data: ^{1}H NMR (C$_6$D$_6$) δ= 0.18 and 0.26 (s, 9H each, Me$_3$Si–), 6.02 and 6.26 (d, J=15.0 Hz, 1H each, HC=) ^{13}C NMR (CDCl$_3$) δ=−1.1 and −0.3 (Me$_3$Si–), 98.5 and 105.1 (≡C–), 124.6 and 146.0 (=C–); MS m/z 196 (M$^+$); IR (Neat) 2160 cm^{-1} ($\nu_{C\equiv C}$).

Dimerizaton of HC≡CSiMe$_3$ to Me$_3$SiCH=C=C=CHSiMe$_3$. A solution of Ru(cod)(cot) (33 mg, 0.1 mmol), PPh$_3$ (160 mg, 0.6 mmol), and HC≡CSiMe$_3$ (3 ml, 340 mmol) in hexane (15 ml) was kept in a refrigerator (−10°C) for 30 h. The solvent and the excess acetylene were evaporated at 10 mmHg. The residue was attached to a vacuum line and the volatile material was distilled at room temperature. The pale yellow solution of the dimer (1.91 g, 92%) had the isomer distribution described in the text. When the reaction was carried out at room temperature, a slight decrease in the *Z*/*E* ratio of butatriene was observed. (*Z*)-Me$_3$SiCH=C=C=CHSiMe$_3$ and (*E*)-Me$_3$SiCH=C=C=CHSiMe$_3$ gave the same spectra.

Selected Spectroscopic Data: ^{1}H NMR (C$_6$D$_6$) δ=0.15 (s, 18H, Me$_3$Si–) and 6.42 (s, 2H, HC=); ^{13}C NMR (CDCl$_3$) δ=−1.13 (Me$_3$Si–), 121.22 (=CHSi–) and 182.99 (=C=); MS m/z 196 (M$^+$); IR (Neat) 1580 cm^{-1} ($\nu_{C=C}$). Their steric identification was by comparison of their GC with those of (*Z*)- and (*E*)-1,4-di-butylbutatriene where the *E*-isomer has a shorter retention time (OV-1 capillary, 30 m).[2]

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