NOTIZEN

Photocatalytic 1,4-Hydrosilation of 1,3-Butadiene with Triethylsilane

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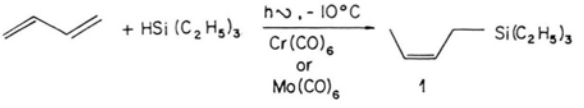
Chromium and molybdenum carbonyl photocatalyzed hydrosilation of 1,3-butadiene by triethylsilane yields exclusively the 1,4-adduct, *cis*-1-triethylsilyl-2-butene which has been fully characterized. Mechanistic possibilities for photocatalytic hydrosilation reactions have been put forward.

The addition reactions of hydrosilanes to multiple bonds (hydrosilation) have proved to be important for the industrial production of organosilicon compounds. This fact and the importance of hydrosilation in the preparation of useful organosilicon reagents in synthetic organic chemistry have prompted us to investigate closely the photocatalytic hydrosilation of olefins, using transition metal complexes. Molybdenum carbonyl photocatalyzed hydrosilation reactions of olefins with trialkylsilanes have not yet been cited in the literature. A short communication [1] reports chromium carbonyl photocatalyzed reactions of conjugated dienes with trimethylsilane, triethoxysilane, and diphenyldihydrosilane to yield 1,4-addition products. Details for the process of isolation and characterization of the adducts have not been given and the use of triethylsilane has been mentioned only for the photocatalytic hydrosilation of *trans*-1,3-pentadiene without any clear and quantified presentation of results [1].

We present here a detailed study of the photocatalytic reaction of 1,3-butadiene with triethylsilane, as a preliminary account of our project on photocatalytic hydrosilation reactions in the presence of hexacarbonylmetal(0) employing various conjugated and non-conjugated dienes. The ultimate goal of this project is to propose a plausible mechanism for such reactions.

In contrast to the relative inertness attributed to triethylsilane in the photocatalytic hydrosilation of conjugated dienes [1], we have found that triethylsilane reacts with 1,3-butadiene to yield *cis*-1-triethylsilyl-2-butene (**1**), under irradiation in the presence of hexacarbonylmolybdenum(0) as well as hexacarbonylchromium(0).



Triethylsilane (9 mmol) in *n*-hexane (100 ml) saturated with 1,3-butadiene at −10 °C has been irradiated (150 W high-pressure Hg arc lamp) in the presence of hexacarbonylchromium(0) or hexacarbonylmolybdenum(0) (0.4 mmol) under an inert gas atmosphere. The reaction was monitored (IR) by following the disappearance of the νSi−H absorption band at 2100 cm^{-1}. The evaporation of the solvent and the excess butadiene followed by distillation (80 °C/15 torr) yielded (0.67 g, 44% in the case of chromium, 0.25 g, 17% in the case of molybdenum) a liquid which has been identified spectroscopically to be **1.** The ^{13}C-{^1H}-NMR spectrum of **1** in chloroform-d gives six signals at δ = 3.30 (Si−CH_2−**C**H_3), 7.27 (Si−**C**H_2−CH_3), 12.43 (C 1), 12.75 (C 4), 126.41 (C 2) and 120.93 (C 3) ppm. The assignment of these signals is based on the chemical shifts and the off-resonance experiment. The ^1H NMR chemical shifts (δ ppm) and coupling constants (J Hz) of **1** in chloroform-d are as follows: Si−C**H**$_2$−CH_3 0.60 (^3J = 7); Si−CH_2−C**H**$_3$ 1.05 (^3J = 7); allylic CH_2 1.55 (^3J = 5.7); allylic CH_3 1.63 (^3J = 3.8); CH_2−C**H**= 5.46 (^3J = 10.6, ^3J = 3.8); CH_3−C**H**= 5.36 (^3J = 10.6, ^3J = 5.7). MS (EI, 70 eV): 170 [M^+], 115 [$(C_2H_5)_3Si$], 87 [$(C_2H_5)_2SiH$], 59 [$(C_2H_5)SiH_2$]. Both the ^1H and ^{13}C NMR results are in accord with the data reported [2] for *cis*-1-trimethylsilyl-2-butene. The value of 10.6 Hz observed for the coupling between the olefinic protons is the only evidence for the *cis*-geometry of **1.** Values of 10.4 (or 12.0 in CCl_4) [2] and *ca.* 11 Hz [3] have been reported for the trimethylsilyl analogue of **1,** while *trans*-geometries result in higher values for the

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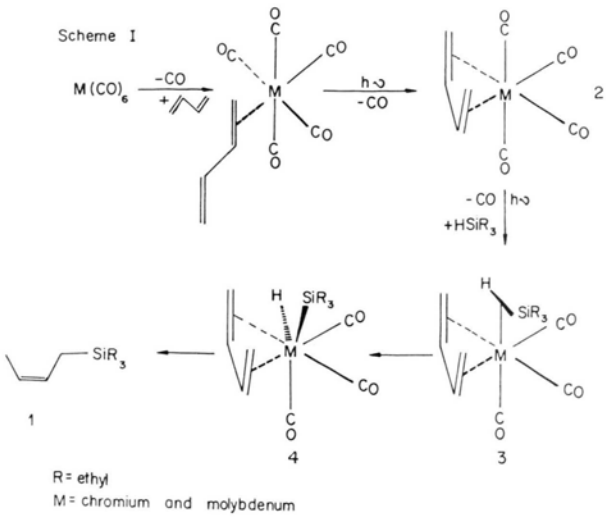

trans-vicinal olefinic coupling (15–18 Hz) [2, 3]. In a separate experiment with a catalyst : substrate ratio of 1:50 turnover numbers of *ca.* 30 and *ca.* 5 have been achieved for hexacarbonylchromium(0) and hexacarbonylmolybdenum(0), respectively.

The exclusive formation of a 1,4-adduct in this photocatalytic reaction encourages one to propose a mechanism similar to one described for the photocatalytic 1,4-hydrogenation of conjugated dienes [4, 5]. In the proposed mechanism (Scheme 1) tetracarbonyl(η^4-1,3-butadiene)metal(0) (**2**) is formed from hexacarbonylmetal(0) and butadiene upon irradiation [6]. Formation of a non-classical complex (**3**) containing an η^2-$HSi(C_2H_5)_3$ ligand may be envisaged [4], although the formation of classical complexes containing hydrido and triethylsilyl ligands which are coordinated to the same metal center, analogous to tricarbonyl(η^4-1,3-butadiene)hydrido-triethylsilylchromium(0) (**4**), is known [7]. The presence of the Si–H moiety (classical or non-classical) in the *fac* position is essential for the formation of a 1,4-adduct. The photolysis of tetracarbonyl(η^4-1,3-butadiene)-chromium(0) in a low temperature matrix has been shown to give predominantly CO dissociation from a *fac* position [8]. This vacant *fac* position may also form in solution and be occupied by a solvent molecule. The solvent may then be replaced, upon further reaction with triethylsilane, to form **4** directly or *via* **3**. **4** eventually collapses to yield **1**. Our continuing studies on the detailed mechanism will enable us to determine whether this collapse would regenerate **2** or **3** in the catalytic cycle.

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