(13), 78 (7), 77 (9), 70 (10), 69 (44), 68 (14), 67 (9), 63 (14), 62 (37), 61 (12), 56 (7) 55 (23), 54 (14), 53 (20), 51 (10), 50 (14); exact mass (EI, measured m/z 125 peak, δ-coniceine, from picrate) calcd for $C_8H_{15}N$ 125.1204, observed 125.1206. Anal. (recrystallized picrate) Calcd for $C_{14}H_{18}N_4O_7$: C, 47.46; H, 5.12; N, 15.81. Found: C, 47.20; H, 5.01; N, 15.69.

Registry No. 5a, 86864-51-9; **5b**, 86864-57-5; **5c**, 86864-53-1; **5d**, 86884-96-0; **5e**, 86884-97-1; **5f**, 86864-58-6; **5g**, 86864-55-3; **5h**, 86864-54-2; **6**, 24165-03-5; **7**, 968-39-8; **8a**, 79425-06-2; **8b**, 726-25-0;

8c, 722-03-2; **8d**, 86884-98-2; **8e**, 86884-99-3; **8f**, 86885-00-9; **11**, 86885-01-0; **12**, 86885-02-1; **13**, 86885-03-2; **14**, 86885-04-3; **15**, 86885-05-4; **16**, 13618-93-4; **16** picrate, 5210-66-2; TrOOTr, 596-30-5; HCl, 7647-01-0; NaOH, 1310-73-2; NaBH₄, 16940-66-2; NaAlH₂Et₂, 17836-88-3; LiAlH₄, 16853-85-3; H₂, 1333-74-0; PhNCS, 103-72-0; *n*-decylamine, 2016-57-1; benzylamine, 100-46-9; cyclohexylamine, 108-91-8; *tert*-butylamine, 75-64-9; piperidine, 110-89-4; 2,2,6,6-tetramethylpiperidine, 768-66-1; *m*-chloroperbenzoic acid, 937-14-4; pyridinium chlorochromate, 26299-14-9; Collins reagent, 20492-50-6.

Notes

Improved Synthesis of Selenophene

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Introduction

The use of aluminum oxide as a packing material or support of 450 °C hot columns in the preparation of selenophene from elemental selenium and acetylene gas has dramatically improved the overall yields obtained from prior methods.[1,2] In particular, a recent study of a semi-large-scale method for selenophene using aluminum oxide support revealed that seven batches are required in order to sufficiently condition the support (~8 h/batch) before yields of about 58% can be achieved.[2] Typically, the first four or five batches provide extremely low yields, requiring a long "incubation" time before the reaction becomes sufficiently efficient. During this conditioning, the alumina becomes coated with carbonaceous material, and simultaneously the yields of selenophene increase. We have now found that inert support materials like sand or glass beads assure a high (70%) yield from the start, thus pointing out that alumina does not have a catalytic effect upon the selenophene synthesis, rather it seems to affect the reaction negatively, therefore requiring initial passivation.

Experimental Section

The reaction between selenium and acetylene with various supports was carried out in glass tubes of 25 × 600 mm, as previously described.[2] These were cleaned prior to use with hot concentrated nitric acid and then rinsed with distilled water and acetone. The glass beads (1-mm diameter) and sand (1-3-mm diameter) were similarly cleaned. The tubes were typically loaded with 120 g of support, and these were preheated and maintained at 450 °C for 3 h under nitrogen until all moisture was removed. The sand or glass beads so treated were then mixed thoroughly with 20-25 g (1-2-mm diameter) of selenium each, and the reloaded tubes were placed back into the oven slightly inclined to facilitate collection of the reaction product. A stream of nitrogen was passed through each tube until 400 °C was reached. Then the nitrogen was replaced with acetylene with a flow rate of 0.25

cm³ s⁻¹, upon which liquid selenophene started to form almost immediately. The temperature was increased slowly to 450 °C and a red liquid (selenophene containing dissolved selenium) was collected during 16 h. During the reaction, the excess acetylene gas was passed through a saturated KOH solution in order to trap any H₂Se. At the end of the reaction, acetylene was replaced with a nitrogen stream, the tubes were allowed to cool, and the glass beads or sand from each tube were then mixed homogeneously with a new portion of 20-25 g of selenium. The tubes were reloaded, and the reaction was restarted, as described above. The crude products from three batches were combined and distilled to give selenophene in 70% yield (based upon the total amount of selenium), bp 109–112 °C (Gronowitz et al.[2] reported bp 105–120 °C). The yields were the same with use of either support, and the product was confirmed via NMR. The crude product also contained ca. 3% toluene, and the residue from the distillation pot contained elemental Se, diphenyl selenide (according to mass spectral data), and other unidentified, high-boiling products.[3]

Results and Discussion

The combined yields of selenophene obtained from three initial batches using glass beads or sand were 70% in either case. Gronowitz et al. reported a combined yield of the first three batches of ca. 8% using aluminum oxide support.[2] They were able to obtain a single batch yield of 58% only after seven batches. Also, all of the supports used here were similarly coated with carbonaceous material. The fact that selenophene forms almost immediately when the reaction is started implies that these carbonaceous coatings, which have been previously suggested to exert a catalytic effect,[1b] in fact, appear to play no catalytic role in the formation of selenophene at all. Moreover, the formation of such carbonaceous material is a common phenomenon in pyrolysis reactions.

These data suggest that the formation of selenophene from selenium and acetylene requires no catalyst, but rather a support that provides an increased surface area to facilitate the reaction, as previously asserted by Gronowitz et al.[2] Thus, we believe that selenium distributes over the surface of the support materials during heating in the glass tube, thereby giving a much greater cross section for reaction with acetylene. However, the nature of the support material itself is also of importance. The comparatively low yields obtained using aluminum oxide as opposed to glass beads or sand bears this out. This may be attributed to the countercatalytic properties of aluminum oxide, which apparently has a destructive effect upon product formation, especially in the initial runs until

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(3) S. Gronowitz, A. Konar, and A.-B. Hörnfeldt, *Chem. Scripta*, **10**, 159 (1976).

such time is reached, when the conditioning of aluminum oxide (after six or seven batches) suppresses this negative effect. Thus, the use of inert support materials achieves higher yields in shorter times. The conversion of selenium into selenophene is almost quantitative (based on selenium), since any unreacted selenium in one batch can be converted into selenophene in the next batch.

Registry No. Selenium, 7782-49-2; acetylene, 74-86-2; selenophene, 288-05-1.

Highly Chemoselective Reductions with PMHS and Palladium(0) Catalyst

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Transition-metal catalysts not only enhance reaction rates but very often significantly change the course of the uncatalyzed reaction, leading to different, and on occasion to completely opposite, regio- and stereochemical selectivities. The catalyzed reaction often also shows increased functional specificity, leading to enhanced chemoselectivity.[1]

The best examples of these properties of transition-metal catalysis are probably found in the literature of organic reduction chemistry, which is still a challenging and demanding area in synthetic chemistry, particularly when working with compounds having several reducible moieties. Fortunately, an astute choice of reducing agent and catalyst can often lead to sufficient chemoselectivity for practical synthesis, without resorting to complex masking procedures. In our recent work, tributyltin hydride reducing agent and $Pd(PPh_3)_4$ catalyst[2,3] were shown to selectively reduce allylic heterosubstituents and Michael acceptors in the presence of other easily reducible functionalities such as benzylic heterosubstituents, aldehydes, and ketones.

In this paper we report on a reducing system that has even greater chemoselectivity and can differentiate unprecedently between functional groups with a similar tendency to be reduced. It involves a Pd(0) catalyst and polymethylhydrosiloxane[4] (PMHS) as a hydride donor.

Surprisingly, although PMHS has been known and readily available for more than 35 years,[5] it has been almost entirely overlooked by organic chemists. There are only sporadic reports on its having been employed for reduction,[6] and then mainly to generate trialkyltin hydrides.[7] A closely related organosilicone olygomer, HSL-94, has been employed for ionic hydrogenation of alkenes, aldehydes, and ketones.[8]

Although in general PMHS is a much weaker reducing agent than tributyltin hydride, when it is used to reduce
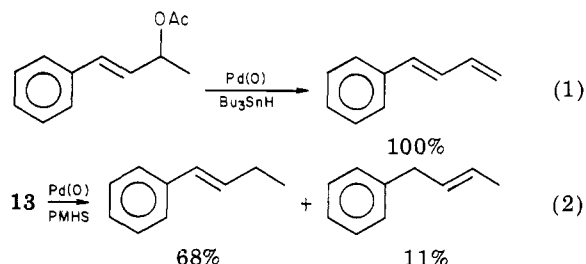
(π-allyl)palladium intermediates it operates with equal efficiency, giving rise to reductive cleavage of allylic heterosubstituents[9] as shown in Table I.

PMHS is a more convenient reagent than Bu_3SnH, as it is more stable,[4] nontoxic,[10] and even less expensive. Moreover, it may be added to a reaction mixture in a single portion, and products are easily separated from the resulting polysiloxane byproducts by filtration or distillation.

It is important to note that this reaction may be carried out with palladium catalysts other than $Pd(PPh_3)_3$. It is conceivable, for example, that under reducing conditions, a Pd(0) catalyst may be generated in situ from a Pd(II) species. Indeed, identical synthetic results were obtained with $Pd(OAc)_2$ and triphenylphosphine at a 1:4 equivalent ratio were substituted for $Pd(PPh_3)_4$.

A study comparing the characteristics of PMHS and Bu_3SnH as hydride donors has revealed striking differences between the two, with PMHS offering much greater chemoselectivity. We point out four of the most significant findings.

A. Higher Selectivity with Regard to β-Hydride Elimination. Tributyltin hydride, a hydride donor of low basicity, is capable of reducing a large variety of multifunctional allylic heterosubstituents.[2] However, compounds possessing a relatively acidic hydrogen α to the allylic unit are incompatible with even this low basicity donor. In such compounds, the intermediate (π-allyl)-palladium complex undergoes β-hydride elimination to yield the corresponding diene,[11] as shown in eq 1. When PMHS was employed, however, reduction of the allylic acetate was clean, with no apparent β-hydride elimination (eq 2).

B. Higher Stability of Both Hydride Donor and Catalyst. Reduction of allylic heterosubstituents with $Bu_3SnH/Pd(0)$ is efficient, particularly when formation of the (π-allyl)palladium intermediate is relatively fast at room temperature. However, when its formation is slow (e.g., when the allylic unit is sterically crowded), both catalyst and tributyltin hydride may deteriorate via competing processes, as indicated by evolution of hydrogen gas and precipitation of metallic palladium. This complication occurs when slow-reacting substrates such as geranyl acetate are reacted with Bu_3SnH. However, when PMHS is employed as the reducing agent, the reaction proceeds as expected (eq 3). Moreover, no gas evolution or color change was observed when solutions containing PMHS and $Pd(PPh_3)_4$ were stirred at room temperature for several days.

C. Differentiation between Allylic Heterosubstituent and Michael Acceptor. Electron-deficient double

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