Pergamon

Tetrahedron Letters 39 (1998) 6335–6336

TETRAHEDRON LETTERS

Initiation of Tin-Mediated Radical Reactions by Diethylzinc-Air

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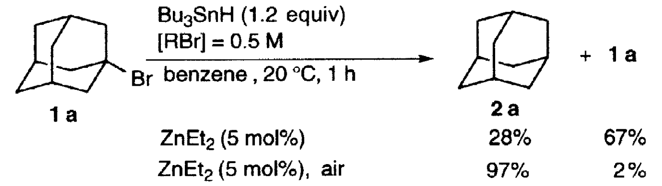
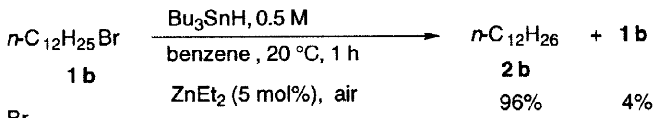
Received 4 June 1998; revised 22 June 1998; accepted 26 June 1998

***Abstract*:** Diethylzinc-air system can serve as an initiator of tin hydride mediated radical reactions of organic halides.

The notable progress in the field of the stereoselective free-radical reactions[1] necessitates a wide variation of steady free-radical initiators capable of initiating radical reactions even at low reaction temperatures. However, in reality, triethylborane-air system[2] is mostly used with a few exceptions.[3] It was previously known that the autoxidation system of diethylzinc can initiate the polymerization of alkenes or facilitate cyclopropanation by a radical mechanism.[4] With this result, we set out to investigate the potential of diethylzinc-air system as a radical initiator. We report herein that diethylzinc-air system is useful for the initiation of tin-mediated radical reactions of organic halides.



(1)



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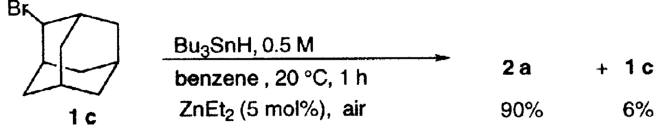

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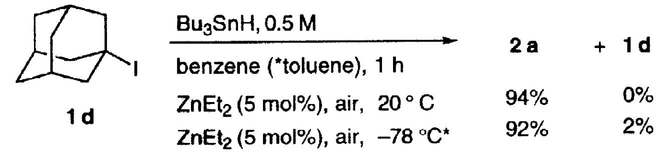

(4)

When a 0.5 M benzene solution of 1-bromoadamantane (**1a**) was treated with 1.2 equiv of tributyltin hydride and 5 mol% of diethylzinc[5] at 20 °C, adamantane (**2a**) was formed in only 28% yield, with a large amount of **1a** remaining (eq 1). The introduction of air, by bubbling, dramatically increased the yield of **2a** to 97%. Comparable results were obtained with THF, ether, and CH_2Cl_2 as solvents, but addition of 10 mol% of HMPA, which can coordinate to diethylzinc, to benzene resulted in low conversions. By a similar procedure, 1-bromododecane (**1b**) and 2-bromoadamantane (**1c**) were efficiently reduced to give dodecane (**2b**) and

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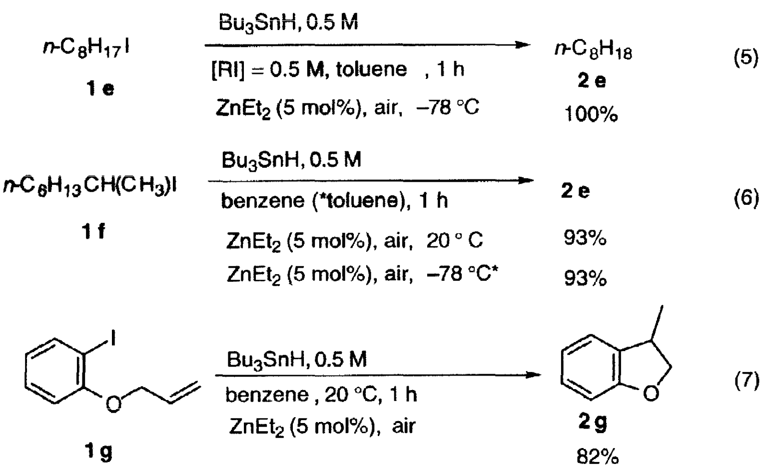
PII: S0040-4039(98)01345-8



adamantane (**2a**), respectively (eqs 2 and 3).[6] In general, the chain propagation of alkyl iodides is more efficient than alkyl bromides due to the weaker C-I bonds. As one would thus anticipate from this, the reduction of 1-iodoadamantane (**1d**) at rt and -78 °C proceeded smoothly (eq 4). Similarly, primary and secondary alkyl iodides **1e** and **1f** were reduced to give octane (**2e**) (eqs 5 and 6). Benzofuran **2g** was obtained from **1g** in 82% yield via a five-membered radical ring closure (eq 7). Oxygen alone can initiate the reaction, but side reaction leading to alcohols inevitably appears: for example, treatment of a 0.5 M benzene solution of **1d** with tin hydride under air bubbling at 20 °C for 1 h resulted in the formation of adamantane (41%) and 1-adamantanol (10%) along with unreacted **1d** (41%).[7]

Consequently, our results indicate that the diethylzinc-air system can serve as an initiator of conventional tin hydride mediated radical reactions and it is anticipated that this initiation system could also be applied to other radical reaction systems.[8]

References and Notes

1. a) Curran, D. P.; Porter, N. A.; Giese, B. *Stereoselectivity of Radical Reactions*; VCH: Weinheim, 1995. b) Smadja, W. *Synlett* **1994**, 1-26. c) Guindon, Y.; Jung, G.; Guérin, B.; Ogilvie, W. W. *Synlett* **1998**, 213-220.
2. a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547-2539. b) Nozaki, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3465-3467.
3. Initiation by sonication or electrolysis, see: a) Nakamura, E.; Imanishi, Y.; Machii, D. *J. Org. Chem.* **1994**, *59*, 8178-8786. b) Tanaka, H.; Ogawa, H.; Suga, H.: Torii, S. *J. Org. Chem.* **1996**, *61*, 9402-9408.
4. a) Furukawa, J.; Kawabata, N. *Adv. Organomet. Chem.* **1974**, *12*, 83-134. b) Sakata, R.; Tsuruta, T.; Saegusa, T.; Furukawa, J. *Kogyo Kagaku Zasshi* **1960**, *63*, 1817-1822. c) Lal, J. *J. Polym. Sci., Part A-1* **1966**, *4*, 1163-1177. d) Miyano, S.; Yamashita, J.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1946. e) Rousseau, G.; Slougui, N. *J. Am. Chem. Soc.* **1984**, *106*, 7283-7285.
5. Commercially available 1 M hexane solution of $ZnEt_2$ (Aldrich) was used for this study.
6. In the comparison experiments using 5 mol% of an initiator, 2-bromonorbornane (**1h**), and tributyltin hydride (20 °C, 1 h), BEt_3-air gave a 96/4 ratio of norbornane/**1h**, whereas $ZnEt_2$-air gave a 82/18 ratio.
7. For aerobic radical reaction mediated by tin hydride leading to alcohols, see: Nakamura, E.; Inubushi, T.; Aoki, S.; Machii, D. *J. Am. Chem. Soc.* **1987**, *113*, 8980-8982.
8. In the initiation step, ethyl and ethylperoxy radicals, generated from diethylzinc by oxidation with oxygen, may abstract hydrogen from tin hydride to generate tin radical. For behaviors of ethylperoxyzincs generated from $ZnEt_2$ and O_2, see: a) Abraham, M. H. *J. Chem. Soc.* **1960**, 4130-4135. b) Yamamoto, K.; Yamamoto, N. *Chem. Lett.* **1989**, 1149-1152. c) Enders, D.; Zhu, J.; Raabe, G. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1725-1728. d) Sosnovsky, G.; Brown, J. H. *Chem. Rev.* **1966**, *66*, 529-566. e) Davies, A. G.; Roberts, B. P. *J. Chem. Soc., B* **1968**, 1074-1078.