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TRIETHYLBORANE-INDUCED RADICAL ADDITION OF ALKYL IODIDES TO ACETYLENES

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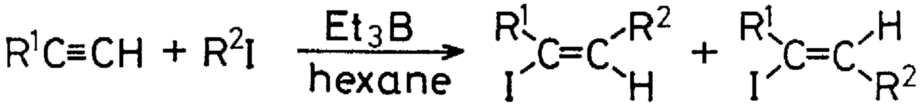
Abstract: Treatment of terminal acetylenes ($R^1C{\equiv}CH$) with secondary or tertiary alkyl iodides (R^2I) in the presence of triethylborane provides the corresponding alkenyl iodides ($R^1C(I){=}CHR^2$) in good yields.

Recently, much attention has been paid to free radical reactions for the synthesis of organic molecules.[1] The intramolecular atom transfer addition of alkyl iodides to properly located triple bond has been widely studied.[2] In contrast, there has been little investigation of intermolecular addition.[3] We have reported that alkyl radical is easily generated from alkyl iodide by means of triethylborane and adds to methyl vinyl ketone to give boron enolate.[4] Here we report further exploitation of triethylborane-induced radical reaction for the addition of alkyl iodides to non-activated alkynes as well as activated alkynes.

Triethylborane (1.0 M hexane solution, 0.5 ml, 0.5 mmol)[5] was added to a solution of trimethylsilylacetylene (0.49 g, 5.0 mmol) and cyclohexyl iodide (0.21 g, 1.0 mmol) at 25°C under an argon atmosphere. The resultant mixture was stirred at 25°C for 6.5 h and then concentrated under reduced pressure. The residual oil was submitted to preparative thin layer chromatography on silica gel to give (Z)-1-iodo-1-trimethylsilyl-2-cyclohexylethene (0.27 g)[6] in 88% yield.

The representative results are summarized in Table 1. Several comments are worth noting. (1) It is essential to use hexane as a solvent. Reaction did not proceed in benzene, dichloromethane, ether, or tetrahydrofuran. (2) The addition of alkyl iodide took place at room temperature for the activated acetylenes (Run 7-13). On the other hand, the hexane solution had to be heated to 60°C for the reaction of non-activated alkynes (Run 14-17). (3) The reaction proceeded regioselectively but nonstereoselectively with the exception of the reaction of trimethylsilylacetylene and triphenylstannylacetylene. For instance, the addition of t-butyl iodide to 1-dodecyne gave a mixture of (E)- and (Z)-2,2-dimethyl-4-iodo-3-tetradecene (E/Z = 77/23). (4) Trimethylsilylacetylene is an excellent substrate for the addition of alkyl iodides. Not only secondary and tertiary alkyl

Table 1. Triethylborane induced radical addition of alkyl iodides to acetylenes[a]

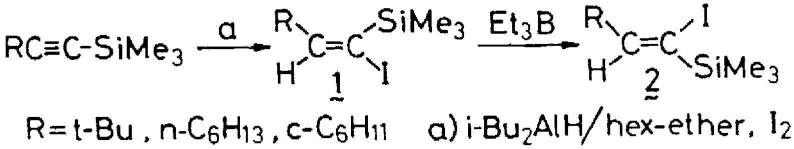


Run	Acetylene R^1	R^2I	Reaction Conditions Temp(°C)	Time(h)	Product $Y(\%)^b$	E/Z
1	Me_3Si	EtI	25	7.5	84	0/100
2		$n\text{-}C_6H_{13}I^c$	25	7.5	85	0/100
3		i-PrI	25	6.5	79^d	0/100
4		cyclohexyl iodide	25	6.5	88^d	0/100
5		Me_3SiCH_2I	25	6.5	66^d	0/100
6		t-BuI	25	6.5	80	0/100
7	COOEt	i-PrI	25	4.0	88	34/66
8		cyclohexyl iodide	25	4.0	90	23/77
9		t-BuI	25	3.0	81	92/8
10	Ph	i-PrI	25	11.0	81	21/79
11		cyclohexyl iodide	25	11.5	72	17/83
12		Me_3SiCH_2I	25	11.0	60	11/89
13		t-BuI	25	11.0	58	81/19
14	$THPOCH_2$	t-BuI	60	12.0	40	60/40
15	$HOCH_2CH_2CH_2$	t-BuI	60	12.0	46	85/15
16	$n\text{-}C_{10}H_{21}$	i-PrI	60	16.0	34	31/69
17		t-BuI	60	20.0	41	77/23
18	Ph_3Sn	i-PrI	25	12.0	53	0/100
19		t-BuI	25	12.0	44	0/100

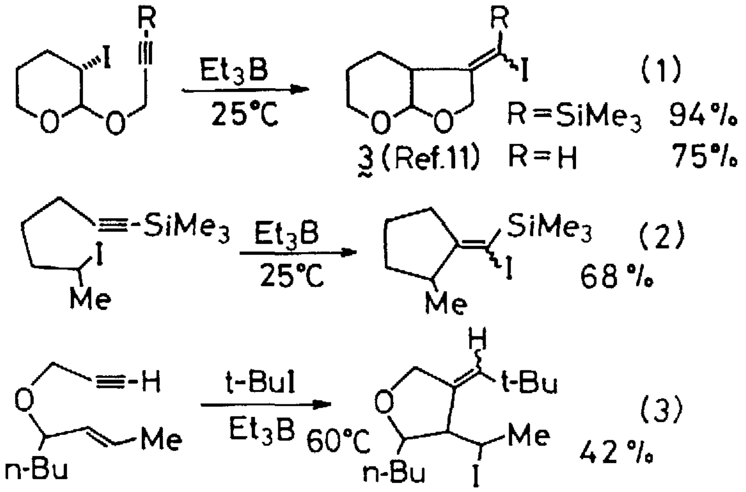
a) Trimethylsilylacetylene (5.0 mmol), alkyl iodide (1.0 mmol), and Et_3B (0.5 mmol) were employed (Run 1-6). Acetylene (1.0 mmol), alkyl iodide (4.0 mmol), and Et_3B (0.5 mmol) were employed (Run 7-13). Acetylene (1.0 mmol), alkyl iodide (4.0 mmol), and Et_3B (2.0 mmol) were employed (Run 14-19). b) Isolated purified yields based on R^2I (Run 1-6) or acetylenes (Run 7-19). c) $(n\text{-}C_6H_{13})_3B$ was used instead of Et_3B. d) Product was contaminated by small amount of $Me_3SiC(I){=}CHEt$ (<5%).

iodides but also primary iodides easily added to trimethylsilylacetylene to provide the corresponding alkenyl iodides with high regio- and stereoselectivities (Run 1-6). (Z)-1-Iodo-1-trimethylsilyl-2-alkylethenes were obtained exclusively upon treatment with alkyl iodides such as t-butyl iodide, i-propyl iodides, and ethyl iodide. (5) Triphenylstannylacetylene also easily reacted with alkyl iodides to give (Z)-1-iodo-1-triphenylstannyl-2-alkylethenes. Moreover, tributylstannylacetylene afforded a complex mixture, and no trace of alkenyl iodides was detected.

The exclusive formation of (Z)-1-iodo-1-trimethylsilyl-2-alkylethenes may be attributed to the isomerization of E-isomer into Z-isomer under the reaction conditions.[7] In fact, stirring a hexane solution of (E)-1-iodo-1-trimethylsilyl-3,3-dimethyl-1-butene (**1a**),[8] (E)-1-iodo-1-trimethylsilyl-1-octene (**1b**),[9] or (E)-1-iodo-1-trimethylsilyl-2-cyclohexylethene (**1c**)[8] at 25°C for 5 h in the presence of a catalytic amount of triethylborane gave the corresponding Z-isomer (**2a**,[7] **2b**,[10] or **2c**[7]) quantitatively.



The reaction was successfully applied to the intramolecular addition reactions (eq. 1 and 2) and intermolecular addition-cyclization reaction (eq. 3) shown below.[12]



References and Notes

1. B. Giese, "Radicals in Organic Synthesis," ed by J. E. Baldwin, Pergamon Press Oxford (1986).
2. D. P Curran, M.-H. Chen, and D. Kim, J. Am. Chem. Soc., **108**, 2489 (1986); D. P. Curran, Synthesis, **1988**, 417, 489 and references cited therein.
3. D. P. Curran describes in his review that secondary and tertiary alkyl iodides add to activated alkynes (See ref. 2).
4. K. Nozaki, K. Oshima, and K. Utimoto, Tetrahedron Lett., **29**, 1041(1988).
5. We thank Toyo Stauffer Chemical Company for the gift of Et_3B.
6. (Z)-1-iodo-1-trimethylsilyl-2-cyclohexylethene: Bp 100°C (bath temp)/1 Torr; IR (neat) 2922, 2846, 1600, 1448, 1247, 910, 867, 840, 810 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.15 (s, 9H), 0.90-1.50 (m, 6H), 1.50-1.80 (m, 4H), 2.25-2.50 (m, 1H), 5.87 (d, J = 7.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ -1.31, 25.59, 25.99, 31.18, 47.49, 110.4, 152.4. Found: C, 43.16; H, 7.09%. Calcd for $C_{11}H_{21}ISi$: C, 42.86; H, 6.87%.
7. Isomerization of (E)-1-iodo-1-trimethylsilyl-2-cyclohexylethene into Z-isomer through the intermediacy of 1-lithio-1-trimethylsilyl-2-alkylethene has been reported. G. Zweifel, R. E. Murray, and H. P. On, J. Org. Chem., **46**, 1292 (1981).
8. G. Zweifel and W. Lewis, J. Org. Chem., **43**, 2739 (1978); J. J. Eisch and G. A. Damasevitz, ibid., **41**, 2214 (1976); K. Uchida, K. Utimoto, and H. Nozaki, ibid., **41**, 2215 (1976).
9. **1b:** Bp 90°C (bath temp)/1 Torr; IR (neat) 2952, 2922, 2852, 1590, 1459, 1249, 840, 756 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ0.25 (s, 9H), 0.80-1.00 (m, 3H), 1.15-1.50 (m, 8H), 1.95-2.15 (m, 2H), 7.16 (t, J = 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ1.15, 14.02, 22.52, 28.74, 29.09, 31.57, 35.14, 106.3, 156.6. Found: C, 42.76; H, 7.39%. Calcd for $C_{11}H_{23}ISi$: C, 42.58; H, 7.47%.
10. **2b:** Bp 90°C (bath temp)/1 Torr; IR (neat) 2954, 2922, 2852, 1602, 1459, 1261, 1248, 870, 839, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ0.15 (s, 9H), 0.80-1.00 (m, 3H), 1.10-1.60 (m, 8H), 2.15-2.30 (m, 2H), 6.10 (t, J = 6.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$)δ-1.43, 14.03, 22.52, 27.82, 28.86, 31.62, 38.89, 113.2, 147.7. Found: C, 42.85; H, 7.69%. Calcd for $C_{11}H_{23}ISi$: C, 42.58; H, 7.47%.
11. **3** (R = H, Mixture of E and Z isomer). Major isomer: bp 45°C (bath temp)/1 Torr; ^{1}H-NMR ($CDCl_3$) δ1.20-1.50 (m, 1H), 1.50-1.80 (m, 1H), 1.80-2.20 (m, 2H), 2.71 (br.s, 1H), 3.46 (ddd, J = 11.7, 10.7, 2.5 Hz, 1H), 3.89 (br.d, J = 11.7 Hz, 1H), 4.40 (ddd, J = 14.4, 2.6, 1.6 Hz, 1H), 4.48 (ddd, J = 14.4, 2.5, 2.4 Hz, 1H), 5.35 (d, J = 3.7 Hz, 1H), 5.96 (ddd, J = 5.2, 2.6, 2.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ150.6, 102.3, 75.39, 67.08, 64.37, 44.91, 22.60, 20.40. Found: C, 36.37; H, 4.25%. Calcd for $C_8H_{11}IO_2$: C, 36.11; H, 4.17%. Minor isomer: 105-110°C (bath temp)/15.5 Torr; ^{1}H-NMR ($CDCl_3$)δ1.20-1.80 (m, 3H), 1.90-2.20 (m, 1H), 2.60-2.80 (m, 1H), 3.70-3.80 (m, 1H), 3.80-4.00 (m, 1H), 4.30 (dd, J = 13.4, 1.8 Hz, 1H), 4.56 (ddd, J = 13.4, 1.7, 1.6 Hz, 1H), 5.28 (d, J = 3.8 Hz, 1H), 5.94 (ddd, J = 3.5, 1.8, 1.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ152.52, 99.91, 68.46, 67.14, 61.47, 43.92, 22.17, 21.98.
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