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Triethylaluminum- or Triethylborane-Induced Free Radical Reaction of Alkyl Iodides and α,β-Unsaturated Compounds

Jing-Yuan Liu,† Yoeng-Jiunn Jang,† Wen-Wei Lin,† Ju-Tsung Liu,‡ and Ching-Fa Yao*,†

Department of Chemistry, National Taiwan Normal University, 88, Section 4, Tingchow Road, Taipei, Taiwan 116, ROC, and Army Force of Military Police School, P.O. Box 90092, Wugu, Taipei, Taiwan 248, ROC

cheyaocf@scc.ntnu.edu.tw

Received November 4, 2002

A series of α,β-unsaturated compounds, **1a**−**c**, **9**, **13**, and **17**, were used as reactants in free radical conjugate addition reactions with different radicals generated from alkyl iodides such as **3**, **4**, or **5** in the presence of triethylborane−oxygen in air or via the use of triethylaluminum−benzoyl peroxide as a free radical initiator. When the reactions were carried out using triethylborane−air, the products, in most cases, were clean and were easily purified. However, higher yields of the 1,4-adducts and less side reactions occurred when less reactive substrates were used as Michael acceptors in reactions with triethylaluminum−benzoyl peroxide and alkyl iodide under similar conditions. A mechanism for this is proposed in Scheme 1.

Introduction

Reactions of β-nitrostyrenes with organometallic reagents such as dialkylzinc[1a] or organozinc halides,[1b,c] *t*-BuHgX/KI,[2] organomanganese,[3] trialkylaluminum or dialkylaluminum chloride,[4] trialkylgallium,[5] and Grignard reagents[6] lead to the generation of alkenes and/or nitroalkanes or halooximes. A previous study found that medium to high yields of alkenes can be generated when (*E*)-β-nitrostyrenes **1** are reacted with triethylborane in a THF solution under reflux in the presence of a trace of oxygen or by photolysis in the presence of *tert*-butyl peroxide as a radical initiator.[7] These results indicate that β-nitrostyrenes are capable of reacting with different organometallic reagents to generate nitroalkanes or alkenes under different conditions and that the reaction mechanism appears to be a free radical and/or an ionic reaction.[1−7] The 1,4-addition of hydrocarbon substituents to α,β-unsaturated carbonyl compounds is usually achieved using organocuprate reagents.[8,9a−j] Similarly, the use of an organocopper reagent,[9k] an organozincate,[10] an organomanaganese,[11] an organotitanate,[12] or a Grignard reagent[8,13] has been reported. In recent years, a catalytic asymmetric Michael addition promoted by chiral metal complexes has been shown to be an efficient method for enantioselective carbon−carbon bond formation.[14]

Utimoto and Oshima were the first to apply the reaction of triethylborane with oxygen to initiate radical reactions.[15] Over classical initiators, the system Et_3B/O_2 offers the great advantage of being efficient even at low temperature (−78 °C). Organoboranes exhibit a tendency to undergo rapid conjugate addition to various types of

† National Taiwan Normal University.
‡ Army Force of Military Police School.
* Corresponding author.

(1) (a) Seebach, D.; Schafer, H.; Schmidt, B.; Schreiber, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1587. (b) Hu, Y.; Yu, J.; Yang, S.; Wang, J.-X.; Yin, Y. *Synlett* **1998**, 1213. (c) Hu, Y.; Yu, J.; Yang, S.; Wang, J.-X.; Yin, Y. *Synth. Commun.* **1999**, *29*, 1157.
(2) Russell, G. A.; Yao, C.-F. *Heteroat. Chem.* **1992**, *3*, 209.
(3) Namboothiri, I. N. N.; Hassner, A. *J. Organomet. Chem.* **1996**, *518*, 69.
(4) Chu, C.-M.; Liu, J.-T.; Lin, W.-W.; Yao, C.-F. *J. Chem. Soc., Perkin Trans. 1* **1999**, 47.
(5) Han, Y.; Huang, Y.-Z.; Zhou, C.-M. *Tetrahedron Lett.* **1996**, *37*, 3347.
(6) (a) Kohler, E. P.; Stone, J. R. *J. Am. Chem. Soc.* **1930**, *52*, 761. (b) Buckley, G. D. *J. Chem. Soc.* **1947**, 1494.
(7) Yao, C.-F.; Chu, C.-M.; Liu, J.-T. *J. Org. Chem.* **1998**, *63*, 719.
(8) (a) Posner, G. H. *Org. React. (N. Y.)* **1972**, *19*, 1. (b) Lipshutz, B. H.; Wilhelm, R. W.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. (c) Lipshutz, B. H.; Sengupta, S. *Org. React. (N. Y.)* **1992**, *41*, 135. (d) Rossiter, B. E.; Swingle, N. M. *Chem. Rev.* **1992**, *92*, 771. (e) Wipf, P. *Synthesis* **1993**, 537.
(9) (a) Alexakis, A.; Berlan; J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047. (b) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 1351. (c) Lipshutz, B. H. *Synlett* **1990**, 119. (d) Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947. (e) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349. (f) Cliv, D. L. J.; Farina, V.; Beeaulieu, P. *J. Chem. Soc., Chem. Commun.* **1981**, 643. (g) Ibuka, T.; Tabushi, E. *J. Chem. Soc., Chem. Commun.* **1982**, 703. (h) Ibuka, T.; Minakata, H.; Mitsui, Y.; Kinoshita, K.; Kawami, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 1193. (i) Yamamoto, K.; Ogura, H.; Jukuta, J.-I.; Inoue, H.; Hamada, K. *J. Org. Chem.* **1998**, *63*, 4449. (j) Frantz, D. E.; Singleton, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 3288. (k) Rieke, R. D.; Klein, W. R.; Wu, T.-C. *J. Org. Chem.* **1993**, *58*, 2492.
(10) (a) Petrier, C.; Duppy, C.; Luche, J. L. *Tetrahedron Lett.* **1986**, *27*, 3149. (b) Petrier, C.; deSouza Barbosa, J. C.; Duppy, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 5761. (c) Waston, R. A.; Kjonaas, R. A. *Tetrahedron Lett.* **1986**, *27*, 1437. (d) Kjonaas, R. A.; Vawter, E. J. *J. Org. Chem.* **1986**, *51*, 3993. (e) Tuckmantel, W.; Oshima, K.; Nozaki, H. *Chem. Ber.* **1986**, *119*, 1581. (f) Langer, F.; Waas, J.; Knochel, P. *Tetrahedron Lett.* **1933**, *34*, 5261. (g) Jubert, C.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 5425. (h) Musser, C. A.; Richey, H. G. *J. Org. Chem.* **2000**, *65*, 7750.
(11) (a) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1989**, *30*, 3541. (b) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1989**, *30*, 7365. (c) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1990**, *31*, 7423.
(12) (a) Arai, M.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 5489. (b) Arai, M.; Lipshutz, B. H.; Nakamura, E. *Tetrahedron* **1992**, *48*, 5709. (c) Flemming, S.; Kabbara, J.; Nickisch, K.; Neh, H.; Westermann, J. *Tetrahedron Lett.* **1994**, *35*, 6075.
(13) (a) Horiguchi, Y.; Matsuzawa, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 4025. (b) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349. (c) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1990**, *31*, 7425.

10.1021/jo020681b CCC: $25.00
Published on Web 04/19/2003

α,β-unsaturated ketones and aldehydes in the presence of a metal mediator.[16] Without the assistance of a metal mediator,[17] organoboranes also undergo conjugate additions to vinyl ketone,[18a] acrolein,[18b] α-methylacrolein,[18c] α-bromoacrolein,[18c] 2-methylenecyclohexanone,[18d] and quinines[17a−c] by a free radical mechanism,[19,20] and traces of oxygen in the reaction mixture are sufficient to initiate these reactions. Various attempts to extend this reaction to β-substituted α,β-unsaturated carbonyl compounds have been unsuccessful[20,21] unless a radical initiator is used.[21] For example, in the presence of oxygen[22] or diacetyl peroxide[21] or under photolysis,[21] trialkylboranes produce alkyl radicals which can be added to β-substituted α,β-unsaturated carbonyl compounds. Toru and coworkers investigated the setereoselectivity of the conjugate addition of trialkylborane to 2-arylsulfinylcyclopentenone.[23] Interestingly, the use of Et_3B along with an excess of secondary and tertiary alkyl iodides led to the generation of secondary or tertiary radicals which could then participate in free radical reactions.[23]

Reactions of trialkylaluminum or triorganoaluminum−ether complexes with α,β-unsaturated nitroalkenes giving high yields of 1,4-alkylated products have been reported by Pecunioso and Menicagli.[24] In 1974, Ashby reported on the nickel- or copper-catalyzed 1,4-additions to α,β-unsaturated ketones by trimethylaluminum or lithium tetramethylaluminate.[25a] The 1,4-addition of organoaluminum compounds[25] has been reported for the transfer of the cyano group to α,β-unsaturated ketones and esters,[26] of alkynyl[27] and alkenyl groups[28] to enones, of the methyl group in nickel-catalyzed reactions of trimethylaluminum with enones,[25a,29] and of higher alkylaluminum compounds to α,β-unsaturated carboxylic acid derivatives.[30] The Cu-catalyzed Michael-type reaction of trimethylaluminum and triethylaluminum with enones[31,32] and the Ni-catalyzed conjugate addition of trimethylaluminum to sterically hindered enones have also been reported.[31d,33,34]

1n 1973, Kabalka reported the first example of a free radical chain reaction involving trialkylaluminum and cyclohexenone compounds.[35] We also recently reported that medium to high yields of alkenes and/or hydroximoyl chloride can be generated when (*E*)-β-nitrostyrenes are reacted with triethylaluminum or diethylaluminum chloride in diethyl ether solution under reflux in the presence of a trace of oxygen in the nitrogen or by photolysis in the presence of benzoyl peroxide as a radical initiator or in the presence of $MgCl_2$ as the Lewis acid after workup with ice-cold concentrated hydrochloric acid.[36] In addition, triethylaluminum can also be used as a radical initiator to generate different radicals that can further react with β-nitrostyrenes to give substituted products.[37] Here we report that triethylaluminum can be used to activate some Michael acceptors, and surprisingly, it is superior to triethylborane in 1,4-addition reactions with some α,β-unsaturated substrates in some cases.

Results and Discussion

Alkenes with electronegative substituents are more easily attacked by nucleophilic alkyl radicals. For example, the use of 2,2-dicyanoalkene as the substrate in alkylation reactions with organotin,[38] alkylmercury halides,[39] organogallium,[40] or organoindium reagents[40] has been reported. However, most of these reactions require several hours to achieve medium to high yields of

(14) (a) Sasai, H.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1994**, *116*, 1571. (b) Arai, T.; Yamada, Y. M. A.; Yamamoto, N.; Sasai, H.; Shibasaki, M. *Chem.—Eur. J.* **1996**, *2*, 1368. (c) Mori, A.; Danda, Y.; Fujii., T.; Hirabayashi, K.; Osakada, K. *J. Am. Chem. Soc.* **2001**, *123*, 10774. (d) Degrado, S. J.; Mizutani, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, 123, 755. (e) Dieguez, M.; Deerenberg, S.; Pamies, O.; Claver, C.; van Leeuwen, P. W. N. M.; Kamer, P. *Tetrahedron: Asymmetry* **2000**, *11*, 3161. (f) Hanessian, S.; Gomtsyan, A.; Malek, N. *J. Org. Chem.* **2000**, *65*, 5623.

(15) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143.

(16) (a) Sazonova, V. A.; Gerasimenko, A. V.; Shiller, N. V. *Zh. Obshch. Khim.* **1963**, *33*, 1988. (b) Arase, A.; Masuda, Y.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2511.

(17) (a) Hawthorne, M. F.; Reintjes, M. *J. Am. Chem. Soc.* **1965**, *87*, 4585. (b) Kabalka, G. W. *J. Organomet. Chem.* **1971**, *33*, C25. (c) Bieber, L. W.; Rolim Neto, P. J.; Generino, R. M. *Tetrahedron Lett.* **1999**, *40*, 4473. (d) Hawthorne, M. F.; Reintjes, M. *J. Am. Chem. Soc.* **1964**, *86*, 951.

(18) (a) Suzuki, A.; Arase, A.; Matsumoto, H.; Itoh, M.; Brown, H. C.; Rogic, M. M.; Rathke, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 5708. (b) Brown, H. C.; Rogic, M. M.; Rathke, M. W.; Kabalka, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 5709. (c) Brown, H. C.; Kabalka, G. W.; Rathke, M. W.;, Rogic, M. *J. Am. Chem. Soc.* **1968**, *90*, 4165. (d) Brown, H. C.; Rathke, M. W.; Kabalka, G. W.; Rogic, M. M. *J. Am. Chem. Soc.* **1968**, *90*, 4166.

(19) Midland, M. M.; Brown, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1506.

(20) Kabalka, G. W.; Brown, H. C.; Suzuki, A.; Honma, S.; Arase, A.; Itoh, M. *J. Am. Chem. Soc.* **1970**, *92*, 710.

(21) Brown, H. C.; Kabalka, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 712.

(22) Brown, H. C.; Kabalka, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 714.

(23) (a) Toru, T.; Watanable, Y.; Tsusaka, M.; Ueno, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10464. (b) Toru, T.; Watanable, Y.; Mase, N.; Tsusaka, M.; Hayakawa, T.; Ueno, Y. *Pure Appl. Chem.* **1996**, *68*, 711. (c) Mase, N.; Watanable, Y.; Tsusaka, M.; Ueno, Y..; Toru, T. *J. Org. Chem.* **1997**, *62*, 7794. (d) Mase, N.; Watanable, Y.; Toru, T. *J. Org. Chem.* **1998**, *63*, 3899.

(24) (a) Pecunioso, A.; Menicagli, R. *Tetrahedron* **1987**, *43*, 5411. (b) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1988**, *53*, 45. (c) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1989**, *54*, 2391.

(25) (a) Ashby, E. C.; Heinsohn, G. *J. Org. Chem.* **1974**, *39*, 3297. (b) Maruoka, K.; Yamamoto, H., *Angew. Chem., Int. Ed. Engl.* **1985**, *26*, 668.

(26) (a) Nagata, W.; Yoshioka, M. *Org. React. (N. Y.)* **1977**, *25*, 255. (b) Carreno, M. C.; Gonzalez, M. P.; Ribagorda, M. *J. Org. Chem.* **1996**, *61*, 6758. (c) Carreno, M. C.; Gonzalez, M. P.; Ribagorda, M. *J. Org. Chem.* **1998**, *63*, 3678.

(27) (a) Hooz, J.; Layton, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 7320. (b) Schwartz, J.; Carr, D. B.; Hansen, R. T.; Dayrit, F. M. *J. Org. Chem.* **1980**, *45*, 3053. (c) Hooz, J.; Layton, R. B. *Can. J. Chem.* **1973**, *51*, 2098.

(28) (a) Hooz, J.; Layton, R. B. *Can. J. Chem.* **1973**, *51*, 2098. (b) Bernady, K. F.; Floyd, M. B.; Poletto, J. F.; Weiss, M. J. *J. Org. Chem.* **1979**, *44*, 1438. (c) Lipshutz, B. H.; Dimock, S. H. *J. Org. Chem.* **1991**, *56*, 5761. (d) Wipf, P.; Smitrovich, J. H.; Moon, C.-W. *J. Org. Chem.* **1992**, *57*, 3178. (e) Zweifel, G.; Miller, J. A. *Org React. (N. Y.)* **1984**, *32*, 375.

(29) Bagnell, L.; Jeffery, E.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1975**, *28*, 801.

(30) Westermann, J.; Nickisch, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1368. (b) Eur. Pat. Appl. EP 534582, 1993. (c) *Chem. Abstr.* **1993**, *119*, 117611s.

(31) (a) Kabbara, J.; Flemming, S.; Nickisch, K.; Neh, H.; Westermann, J. *Chem. Ber.* **1994**, *127*, 1489. (b) Kabbara, J.; Flemming, S.; Nickisch, K.; Neh, H.; Westermann, J. *Synlett* **1994**, 679. (c) Kabbara, J.; Flemming, S.; Nickisch, K.; Neh, H.; Westermann, J. *Tetrahedron Lett.* **1994**, *35*, 8591. (d) Kabbara, J.; Flemming, S.; Nickisch, K.; Neh, H.; Westermann, J. *Liebigs Ann.* **1995**, 401.

(32) Kabbara, J.; Flemming, S.; Nickisch, K.; Neh, H.; Westermann, J. *Synlett* **1994**, 679.

(33) (a) Flemming, S.; Kabbara, J.; Nickisch, K.; Neh, H.; Westermann, J. *Tetrahedron Lett.* **1994**, *33*, 6075. (b) Flemming, S.; Kabbara, J.; Nickisch, K.; Neh, H.; Westermann, J. *Synthesis* **1994**, 317.

(34) Kunz, H.; Pees, K. J. *J. Chem. Soc., Perkin. Trans. 1* **1989**, 1168.

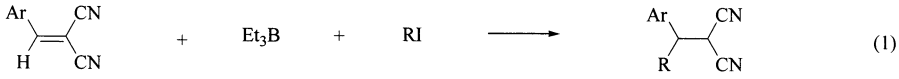
(35) Kabalka, G. W.; Daley, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 4428.

(36) Chu, C.-M.; Liu, J.-T.; Lin, W.-W.; Yao, C.-F. *J. Chem. Soc., Perkin Trans. 1* **1999**, 47.

(37) Liu, J.-Y.; Liu, J.-T.; Yao, C.-F. *Tetrahedron Lett.* **2001**, *21*, 3613.

(38) (a) Mizuno, K.; Ikeda, M.; Toda, S.; Otsuji, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1288. (b) Mizuno, K.; Nakanishi, K.; Tachibana, A.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 344.

TABLE 1. Reaction of 1-Aryl-2,2-dicyanoethenes (1 equiv) with RI (7.5−15 equiv) and Et_3B (4−5 equiv) in THF Solution in the Presence of Oxygen



1 **2a** **3, 4, 5** **6, 7, 8**

a: Ar =Ph
b: Ar = 4-$MeOC_6H_4$
c: Ar = 4-ClC_6H_4

3. R = *i*-Pr
4. R = *c*-C_6H_{11}
5. R = *t*-Bu

6

a: Ar = Ph, R = *i*-Pr
b: Ar = 4-$MeOC_6H_4$, R = *i*-Pr
c: Ar = 4-ClC_6H_4, R = *i*-Pr

7

a: Ar = Ph, R = *c*-C_6H_{11}
b: Ar = 4-$MeOC_6H_4$, R = *c*-C_6H_{11}
c: Ar = 4-ClC_6H_4, R = *c*-C_6H_{11}

8

a: Ar = Ph, R = *t*-Bu
b: Ar = 4-$MeOC_6H_4$, R = *t*-Bu
c: Ar = 4-ClC_6H_4, R = *t*-Bu

entry	**1**	RI (equiv)	product	yield[a] (%)
1	**1a**	**3** (15)	**6a**	99
2	**1b**	**3** (15)	**6b**	99
3	**1c**	**3** (15)	**6c**	100
4	**1a**	**4** (15)	**7a**	95
5	**1b**	**4** (15)	**7b**	95
6	**1c**	**4** (15)	**7c**	100
7	**1a**	**5** (7.5)	**8a**	92
8	**1b**	**5** (7.5)	**8b**	99
9	**1c**	**5** (7.5)	**8c**	100

[a] For the NMR yields DMF was used as an internal standard.

products. Triethylborane not only can be used to generate radical species, but also can be used as an effective radical initiator for generating different radicals by the reaction of triethylborane with an alkyl iodide under mild conditions.[41,42] On the basis of these reports, we attempted to utilize this methodology to react 1-aryl-2,2-dicyanoethenes with radicals using triethylborane and air as the free radical initiator to induce the generation of different radicals from an alkyl iodide. As expected, good to excellent yields (92−100%) of **6**, **7**, or **8** were obtained within 10−30 min when 1-aryl-2,2-dicyanoethenes **1a**−**c** and an excess of the alkyl iodide such as isopropyl iodide (**3**), cyclohexyl iodide (**4**), or *tert*-butyl iodide (**5**) (7.5−15 equiv) were added to the THF solution, after which **2a** (3 equiv) was slowly added at room temperature under similar conditions (eq 1 and Table 1). The products were easily purified by column chromatography, and the spectral data of the known products are also consistent with literature data.[43] The use of an excess of the alkyl iodide and the slow addition of triethylborane are necessary to prevent the formation of ethyl addition products.

Our previous study reported that the substitution of β-nitrostyrenes can also be achieved using triethylaluminum and benzoyl peroxide as the initiator[36a] to induce alkyl radicals from alkyl iodides.[36b] To compare differences in reactivity between triethylaluminum and triethylborane, we also examined the triethylaluminum−benzoyl peroxide system.

Triethylaluminum was reacted with 1-aryl-2,2-dicyanoethenes **1a**−**c** (1 mmol; **a**, Ar = Ph; **b**, Ar = 4-$MeOC_6H_4$; **c**, Ar = 4-ClC_6H_4), benzoyl peroxide (2 equiv), and excess alkyl iodide RI such as **3**, **4**, or **5** (10−15 equiv) in dry diethyl ether at 0 °C for 30 min, after which the solution was stirred at room temperature until all the starting material had disappeared. After the solution was quenched with ice-cold dilute hydrochloric acid solution and ex-

(39) (a) Russell, G. A.; Shi, B. Z.; Jiang, W.; Hu, S.; Kim, B. H.; Bank, W. *J. Am. Chem. Soc.* **1995**, *117*, 3952. (b) Russell, G. A.; Chen, P.; Yao, C.-F.; Kim, B. H. *J. Am. Chem. Soc.* **1995**, *117*, 5967. (c) Russell, G. A.; Yao, C.-F.; Rajaratnam, R.; Kim, B. H. *J. Am. Chem. Soc.* **1991**, *113*, 373

(40) Araki, S.; Horie, T.; Kato, M.; Hirashita, T.; Yamamura, H.; Kawai, M. *Tetrahedron Lett.* **1999**, *40*, 2331.

(41) (a) Suzuki, A.; Nozawa, S.; Harada, M.; Itoh, M.; Brown, H. C.; Midland, M. M. *J. Am. Chem. Soc.* **1971**, *93*, 1508. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (c) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 1041. (d) Bertrand, M. P.; Feray, L.; Nouguier, R.; Perfetti, P. *J. Org. Chem.* **1999**, *64*, 9189. (e) Miyabe, H.; Ushiro, C.; Ueda, M.; Yamakawa, K.; Naito, T. *J. Org. Chem.* **2000**, *65*, 176. (f) Wu, B.; Avery, B. A.; Avery, M. A. *Tetrahedron Lett.* **2000**, *41*, 3797. (g) Miyabe, H.; Ueda, M.; Naito, T. *J. Org. Chem.* **2000**, *65*, 5043. (h) Miyabe, H.; Fujii, K.; Goto, T.; Naito, T. *Org. Lett.* **2000**, *2*, 4071. (i) Yorimitsu, H.; Nakamura, T.; Shinokubo, H.; Oshima, K.; Omoto, K.; Fujimoto, H. *J. Am. Chem. Soc.* **2000**, *122*, 11041. (j) Deprele, S.; Montchamp, J.-L. *J. Org. Chem.* **2001**, *66*, 6745.

(42) (a) Tashtoush, H. I.; Sustmann, R. *Chem. Ber.* **1992**, *125*, 287. (b) Tashtoush, H. I.; Sustmann, R. *Chem. Ber.* **1993**, *126*, 1759. (c) Liu, J.-T.; Jang, Y.-J.; Shih, Y.-K.; Hu, R.-S.; Chu, C.-M.; Yao, C.-F. *J. Org. Chem.* **2001**, *66*, 6021 (d) Yorimitsu, H.; Nakamura, T.; Shinokubo, Oshima, K. *J. Org. Chem.* **1998**, *63*, 8604. (e) Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *J. Org. Chem.* **2001**, *66*, 7776. (f) Fujita, K.; Nakamura, T.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 3137.

(43) (a) Cugny, T.; Normant, J. F. *Bull. Soc. Chim. Fr.* **1961**, 2423. (b) Prout, F. S. *J. Am. Chem. Soc.* **1952**, *74*, 5915. (c) Prout, F. S.; Huang, E. P.-Y.; Hartman, R. J.; Korpics, C. J. *J. Am. Chem. Soc.* **1954**, *76*, 1911. (c) Holmberg, C. *Liebigs Ann. Chem.* **1981**, 748. (d) Gaudemar-Bardone, F.; Mladenova, M.; Gaudemar, M. *Synethesis* **1988**, 611. (e) Yamamoto, Y.; Nishii, S. *J. Org. Chem.* **1988**, *56*, 3597 and references therein.

TABLE 2. Reaction of 1-Aryl-2−2-dicyanoethenes (1 equiv) with RI (10−15 equiv), Et_3Al (4−6 equiv), and Benzoyl Peroxide (2 equiv) in Diethyl Ether at 0 °C for 30 min and Then at Room Temperature

1 **2b** **3, 4, 5** **6, 7, 8**

6 **7** **8**

a: Ar = Ph, R = *i*-Pr **a:** Ar = Ph, R = *c*-C_6H_{11} **a:** Ar = Ph, R = *t*-Bu

b: Ar = 4-$MeOC_6H_4$, R = *i*-Pr **b:** Ar = 4-$MeOC_6H_4$, R = *c*-C_6H_{11} **b:** Ar = 4-$MeOC_6H_4$, R = *t*-Bu

c: Ar = 4-ClC_6H_4, R = *i*-Pr **c:** Ar = 4-ClC_6H_4, R = *c*-C_6H_{11} **c:** Ar = 4-ClC_6H_4, R = *t*-Bu

entry	**1**	RI (equiv)	product	yield[a] (%)
1	**1a**	**3** (10)	**6a**	85
2	**1b**	**3** (10)	**6b**	100
3	**1c**	**3** (10)	**6c**	100
4	**1a**	**4** (10)	**7a**	76
5	**1b**	**4** (10)	**7b**	96
6	**1c**	**4** (10)	**7c**	95
7	**1a**	**5** (10)	**8a**	100
8	**1b**	**5** (10)	**8b**	100
9	**1c**	**5** (10)	**8c**	100

[a] For NMR yields DMF was used as an internal standard.

tracted with dichloromethane, product yields were measured by ^1H NMR, and medium to high (76−100%) yields of the product **6**, **7**, or **8** were observed. These compounds were also easily purified by flash column chromatography as described above (eq 2 and Table 2).

On the basis of the above results, either triethylborane in the presence of air or triethylaluminum in the presence of benzoyl peroxide reacts rapidly and completely with an alkyl iodide under mild conditions. Using a variety of alkyl iodides, such products can be prepared under one-pot conditions. Better and clean results were obtained by the reaction of triethylborane with three different types of 1-aryl-2,2-dicyanoethenes. Ethyl addition products are always generated when the triethylborane solution is added to the alkyl iodide solution too rapidly, thus complicating the purification procedure. When benzylidenemalononitrile was used, the yield of **6a** or **7a** was lower, when the triethylaluminum−benzoyl peroxide system was used (Table 2, entries 1 and 4). Although the yield of the expected product was slightly lower and the reaction rate was also slower compared to those of the triethylaluminum−benzoyl peroxide with triethylborane−air system, the formation of the ethyl addition product was easily avoided provided the triethylaluminum was added slowly to the RI solution.

The regioselective 1,4-addition of alkylidenemalonates can be achieved via the use of several types of organometallic reagents. The reactions of Grignard reagents with α,β-unsaturated carbonyl compounds usually afford 1,2-addition products. However, regioselective 1,4-addition was also reported for reactions of Grignard reagent with alkylidenemalonates and alkylidenecyanoacetates.[43] Similarly, reactions of tetraorganogallate complexes,[44a] dialkylaluminum chlorides,[44b] organomanganese reagents,[44c] triorganogallium,[40] or triorganoindium[40] with alkylidenemalonates also lead to the formation of 1,4-adducts. The first asymmetric conjugate addition of dialkylzinc and triethylaluminum reagents to aryl- and alkylidenemalonates using a catalytic copper/homochiral phosphorus ligand system was also reported by Alexakis.[45]

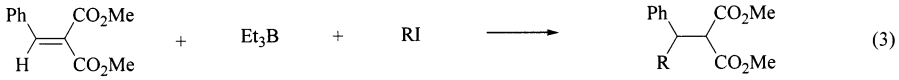
On the basis of the above reports, dimethyl benzylidenemalonate (**9**) was chosen as an alternate Michael acceptor to examine the efficiency of the triethylborane and triethylaluminum systems. As shown in Table 3, the reactions of alkyl halides with this substrate afford only low to medium (25−80%) yields of 1,4-adduct **10**, **11**, or **12** (eq 3 and Table 3, entries 1−3). Dimethyl benzylidenemalonate is not always entirely consumed, even when the amount of triethylborane is increased and the reaction time is extended. In addition, dialkylated products are produced, along with the monoalkylated products, when triethylborane and air as the radical initiator is used. For example, the dialkylated product PhCH(*i*-Pr)-C(*i*-Pr)$(CO_2Me)_2$ (**10a**) could be isolated when isopropyl iodide was used (Table 3, entry 1).

Although low yields of 1,4-adducts were obtained when **9** was reacted with alkyl halide in the presence of triethylborane−air, the system using triethylaluminum and benzoyl peroxide resulted in high yields (91−95%). Fortunately, no dialkylated products were observed, and only high yields of the 1,4-adducts were generated (eq 4 and Table 4). These different results possibly can be explained by the different coordination abilities of triethylborane vis-à-vis triethylaluminum for the same substrate. It is possible that the size of the aluminum atom permits it to coordinate to the oxygen of the substrate more tightly so that the substrates can be

(44) (a) Han, Y.; Huang, Y.-Z.; Fang, L.; Tao, W.-T. *Synth. Commun.* **1999**, *29*, 867. (b) Maas, S.; Stamm, A.; Kunz, H. *Synthesis* **1999**, *10*, 1792. (c) Cahiez, G.; Alami, M. *Tetrahedron* **1989**, *45*, 4163.

(45) Alexakis, A.; Benhaim, C. *Tetrahedron*: *Asymmetry* **2001**, *12*, 1151.

TABLE 3. Reaction of Dimethyl Benzylidenemalonate (1 equiv) with RI (7.5−15 equiv) and Et_3B (4−6 equiv) in THF Solution in the Presence of Oxygen at Room Temperature



9 **2a** **3, 4, 5** **10, 11, 12**

10 : R = *i*-Pr

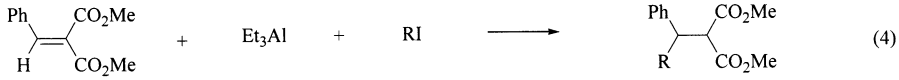
11 : R = *c*-C_6H_{11}

12 : R = *t*-Bu

entry	RI (equiv)	product	yield[a] (%)
1	**3** (15)	**10**	80[b]
2	**4** (15)	**11**	55
3	**5** (7.5)	**12**	25

[a] For NMR yields DMF was used as an internal standard. [b] The crude mixture contains 24% dialkylated product **10a**.

TABLE 4. Reaction of Dimethyl Benzylidenemalonate (1 equiv) with RI (6−10 equiv), Et_3Al (About 6 equiv), and Benzoyl Peroxide (2 equiv) in Diethyl Ether at 0 °C for 30 min and Then at Room Temperature for 1.5−2 h



9 **2b** **3, 4, 5** **10, 11, 12**

3, 10 : R = *i*-Pr

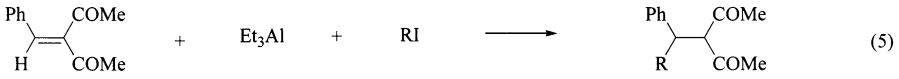
4, 11 : R = *c*-C_6H_{11}

5, 12 : R = *t*-Bu

entry	RI (equiv)	product	yield[a] (%)
1	**3** (10)	**10**	95
2	**4** (10)	**11**	93
3	**5** (6)	**12**	91

[a] For NMR yields DMF was used as an internal standard.

TABLE 5. Reaction of Benzylideneacetylacetone (1 equiv) with RI (7.5−15 equiv), Et_3Al (8−10 equiv), and Benzoyl Peroxide (2 equiv) in Diethyl Ether at Room Temperature for 4−5 h



13 **2b** **3, 4, 5** **14, 15, 16**

14. R = *i*-Pr

15. R = *c*-C_6H_{11}

16. R = *t*-Bu

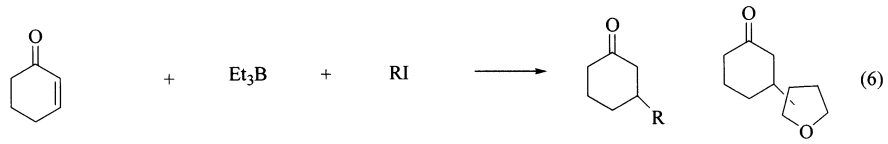
entry	RI (equiv)	product	yield[a] (%)
1	**3** (15)	**14**	50
2	**4** (15)	**15**	81
3	**5** (7.5)	**16**	30

[a] For NMR yields dibromomethane was used as an internal standard.

activated more efficiently and be easily attacked by the nucleophilic alkyl radical.

It has been reported that medium to high yields of conjugate allylation to acceptor **13** can be achieved using triallylgallium or triallylindium.[40] In the case of substrate **13**, the triethylborane system failed to undergo a conjugate addition to this substrate. However, 1,4-addition can be achieved when the triethylaluminum−benzoyl peroxide system (30−81%) is used, but the yields of 1,4-adduct were significantly decreased when the reaction was carried out at 0 °C because of the low activity of substrate **13** (eq 5 and Table 5). However, the yield can be improved

TABLE 6. Reaction of 2-Cyclohexen-1-one (1 equiv) with RI (7.5−15 equiv) and Et_3B (8−10 equiv) in THF Solution in the Presence of Oxygen



17 **2a** **3, 4, 5** **18, 19, 20** **21a, 21b**

18 : R = *i*-Pr

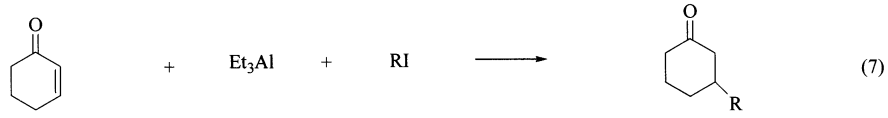
19 : R = *c*-C_6H_{11}

20 : R = *t*-Bu

entry	RI (equiv)	solvent	product	yield[a] (%)
1	**3** (10)	THF	**18**	91
2	**3** (15)	THF/H_2O	**18**	88
3	**4** (15)	THF	**19**	64[b]
4	**4** (15)	THF/H_2O	**19**	67[c]
5	**5** (7.5)	THF	**20**	52[d]
6	**5** (7.5)	THF/H_2O	**20**	64

[a] For NMR yields dibromomethane was used as an internal standard. [b] The yield was calculated by ^{1}H NMR after removing the cyclohexyl iodide and other compounds by flash column chromatography, and a 33% yield of the THF radical addition products **21a** and **21b** was observed. [c] A 32% yield of THF adducts was observed. [d] Traces of THF adducts were observed.

TABLE 7. Reaction of 2-Cyclohexen-1-one (1 equiv) with RI (7.5−15 equiv), Et_3Al (6−10 equiv), and Benzoyl Peroxide (2 equiv) in Diethyl Ether at 0 °C for 30 min and Then at Room Temperature for 0.5−1 h



17 **2b** **3, 4, 5** **18, 19, 20**

18 : R = *i*-Pr

19 : R = *c*-C_6H_{11}

20 : R = *t*-Bu

entry	RI (equiv)	product	yield[a] (%)
1	**3** (10)	**18**	77
2	**4** (10)	**19**	99
3	**5** (10)	**20**	100

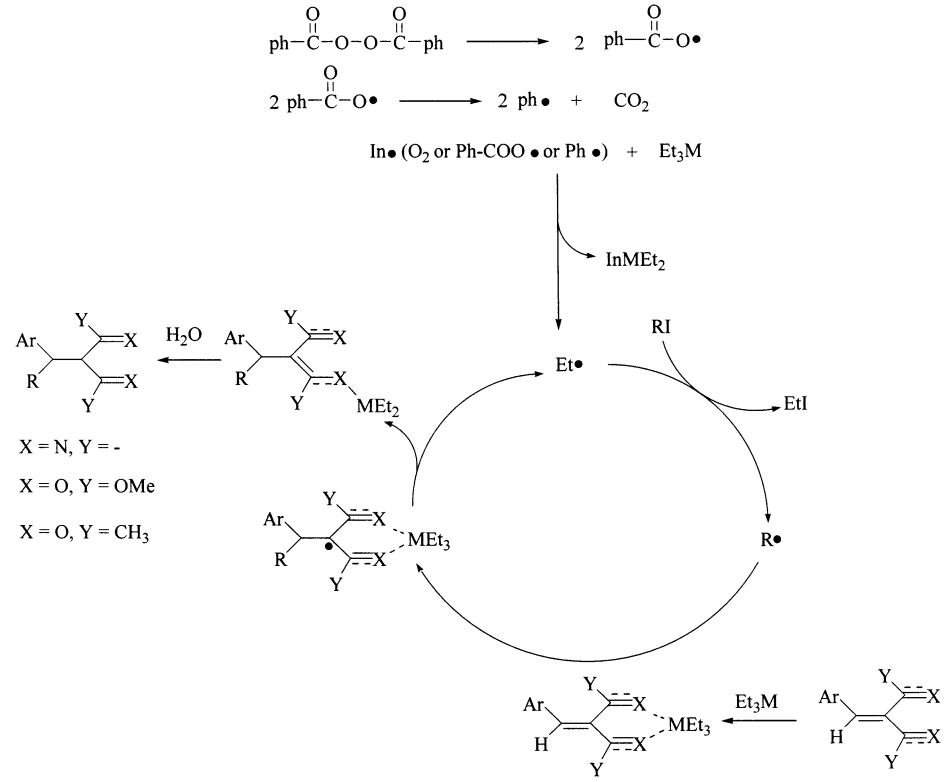
[a] For NMR yields dibromomethane was used as an internal standard. [b] **17** was entirely consumed.

by carrying out the reaction at room temperature for several hours and using larger amounts of triethylaluminum.

The conjugate addition of an enone can be achieved by many types of organometallic reagents. In recent years, the catalytic asymmetric conjugate addition of organometallic reagents to enones has also been reported.[14] Here, we chose 2-cyclohexen-1-one (**17**) as a representative enone to study the difference between the triethylborane and triethylaluminum systems.

Only medium to high yields of product were obtained using the triethylborane system in THF or in THF/H_2O solution (9/1 volume ratio of THF/H_2O) when the substrate was **17**. In the case of isopropyl iodide, the product yield was acceptable (eq 6 and Table 6, entry 1). However, when *tert*-butyl iodide was used as the alkyl halide and 5 equiv of triethylborane was used, the adduct was obtained in only 42% yield, after the mixture was stirred for 30 min in THF solution, and only 52% of the same adduct was obtained when the amount of triethylborane was increased to 10 equiv and the reaction time was extended to several hours (eq 6 and Table 6, entry 5). When the reaction was carried out in THF/H_2O solution, the yield of adduct was increased from 52% to 64% (Table 6, entry 6). Because the ^{1}H NMR spectrum of the cyclohexyl iodide was seriously overlapped with the addition product, the ^{1}H NMR yield of adduct was calculated by isolation after removal of the cyclohexyl iodide and other impurities (Table 6, entry 3). The case where cyclohexyl iodide is used as the radical source is also of interest. From the ^{1}H NMR spectrum, although all the starting material was consumed, only a medium yield of the cyclohexyl addition product was obtained because of the competition of the THF radical addition reaction. An approximate yield of 33% of THF adducts **21a** and **21b** was observed in the cyclohexyl iodide case and only traces of THF adducts were observed in the *tert*-butyl iodide case in the presence or absence of water in the THF solution. This indicates that the *tert*-butyl radical is more reactive than the cyclohexyl radical, and as a result, the yield of the THF adducts **21a** and **21b** was decreased under similar conditions.

SCHEME 1



On the basis of the above observation, the rates of the conjugate addition of the triethylaluminum system to 2-cyclohexen-1-one were faster and the yields of the product were also better than those of the triethylborane system (77−100%). The different coordination ability between aluminum and borane atoms may account for this behavior as describe above (eq 7, Table 7).

In conclusion, we describe an easy method for the synthesis of different products by reactions of α,β-unsaturated compounds with different radicals, prepared from alkyl iodides and triethylborane in the presence of oxygen at room temperature or alkyl iodides and triethylaluminum in the presence of benzoyl peroxide. The use of triethylborane and air to initiate the radical conjugate addition is a good choice, because the reactions are clean and products easily purified. However, when less reactive substrates are used and lower yields of the 1,4-adducts are obtained, triethylborane can be replaced with triethylaluminum to generate the same products. The higher yields of the 1,4-adducts in the triethylaluminum system can be explained by the better coordination ability of the aluminum atom to the less reactive substrate. A mechanism for the above reactions is proposed in Scheme 1.

The application of these two methods could broaden the scope of the utility of organoborane and organoaluminum reagents in organic synthesis.

Experimental Section

General Procedures. All reactions were performed in flame- or oven-dried glassware under a positive pressure of air or nitrogen. Analytical thin-layer chromatography was performed with silica gel 60F glass plates and flash chromatography by use of silica gel 60 (230−400 mesh).

Materials. Triethylborane (**2a**), triethylaluminum (**2b**), 2-iodopropane (**3**), cyclohexyl iodide (**4**), 2-iodo-2-methylpropane (**5**), and 2-cyclohexen-1-one (**17**) were obtained commercially, and other commercially available reagents were used without further purification. The starting materials 1-aryl-2,2-dicyanoethenes **1a**−**c**,[46] dimethyl benzylidenemalonate (**9**),[47] and benzylideneacetylacetone (**13**)[48] were prepared according to literature procedures.

1-Phenyl-2,2-dicyanoethene (1a). This compound was prepared according to literature procedures:[46] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.90 (m, 2H), 7.78 (s, 1H), 766−7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.87, 134.58, 130.93, 130.69, 129.60, 113.65, 112.50, 82.92.

1-(4-Methoxyphenyl)-2,2-dicyanoethene (1b). This compound was prepared according to literature procedures:[46] ^{1}H NMR (400 MHz, CDCl3) δ 7.91 (d, J = 8.8 Hz, 2H), 7.65 (s, 1H), 7.02 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.81, 158.80, 133.41, 124.02, 115.12, 114.38, 113.30, 78.61, 55.77.

1-(4-Chlorophenyl)-2,2-dicyanoethene (1c). This compound was prepared according to literature procedures:[46] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.87 (d, J = 9.0 Hz, 2H), 7.75 (s, 1H), 7.53 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.23, 141.11, 131.80, 130.04, 129.26, 113.40, 112.30, 83.36.

Dimethyl Benzylidenemalonate (9). This compound was prepared according to literature procedures:[47] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.40−7.38 (m, 5H), 3.840 (s, 3H), 3.837 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.07, 164.47, 142.86, 132.76, 130.63, 129.33, 128.83, 125.52, 52.48.

Benzylideneacetylacetone (13). This compound was prepared according to literature procedures:[48] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.40 (s, 5H), 2.43 (s, 3H), 2.29 (s,

(46) Oh, H. K.; Yang, J. H.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2000**, *65*, 2188.
(47) Liao, Y.; Huang, Y.-Z. *Tetrahedron Lett.* **1990**, 31, 5897.
(48) Attanasi, O.; Fillippone, P.; Mei, A. *Synth. Commun.* **1983**, *13*, 1203.

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.46, 196.41, 142.81, 139.76, 132.89, 130.59, 129.64, 128.98, 31.57, 26.45.

Typical Procedures for the Synthesis of 6, 7, or 8 from the Reaction of 1-Aryl-2,2-dicyanoethenes 1a−c (a, Ar = Ph; b, Ar = 4-MeOC$_6$H$_4$; c, Ar = 4-ClC$_6$H$_4$) Alkyl Iodide 3, 4, or 5, and 2a in THF Solution in the Presence of the Oxygen in the Air (Eq 1 and Table 1). In a Pyrex test tube with a magnetic stirrer were placed 1 mmol of 1-aryl-2,2-dicyanoethene **1a**, **1b**, or **1c**, 4 mmol of **2a** (1.0 M in hexane solution), and 7.5−15 mmol of alkyl iodide **3**, **4**, or **5** in 8 mL of THF, and the solution was bubbled with air from a balloon. After 10−30 min, the solvent was evaporated and the oily residue was purified by flash column chromatography to give a 92−100% yield of **6a**−**c**, **7a**−**c**, or **8a**−**c**. In the case of known compounds, all spectral data are consistent with literature reports.[39b,49,50] All experimental results are shown in Table 1.

1,1-Dicyano-3-methyl-2-phenylbutane (6a). The spectral data for this compound are consistent with the literature data:[49] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.30 (m, 5H), 4.16 (d, J = 5.7 Hz, 1H), 2.83 (dd, J = 9.7, 5.7 Hz, 1H), 2.40−2.34 (m, 1H), 1.12 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.59, 129.01, 128.68, 128.21, 112.14, 111.86, 53.29, 30.18, 27.69, 20.80, 20.21; MS *m*/*z* (relative intensity) 198 (M^+, 25), 180 (81), 169 (100), 162 (31); HRMS *m*/*z* calcd for $C_{14}H_{16}N_2O$ 198.1157, found 198.1154.

1,1-Dicyano-3-methyl-2-(4-methoxyphenyl)butane (6b). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 4.14 (d, J = 5.5 Hz, 1H), 3.82 (s, 3H), 2.80 (dd, J = 9.7, 5.5 Hz, 1H), 2.43−2.25 (m, 1H), 1.12 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.78, 129.37, 128.51, 114.38, 112.34, 111.94, 55.15, 52.59, 30.12, 27.87, 20.74, 20.15; MS *m*/*z* (relative intensity) 228 (M^+, 8), 185 (8), 164 (10), 163 (100), 135(9), 121 (92), 91 (15), 77 (17), 55 (20); HRMS *m*/*z* calcd for $C_{14}H_{16}N_2O$ 228.1262, found 228.1260.

1,1-Dicyano-3-methyl-2-(4-chlorophenyl)butane (6c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 4.16 (d, J = 5.6 Hz, 1H), 2.82 (dd, J = 9.8, 5.6 Hz, 1H), 2.40−2.29 (m, 1H), 1.13 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.02, 134.79, 129.60, 129.35, 111.91, 111.52, 52.81, 30.16, 27.64, 20.76, 20.31; MS *m*/*z* (relative intensity) 234 ($(M + 2)^+$, 5) 232 (M^+, 23), 189 (5), 169 (39), 167 (96), 163(68), 153 (23), 139 (15), 125 (100), 115 (25), 103 (7), 89 (13), 73 (9), 55(16); HRMS *m*/*z* found for $C_{13}H_{13}N_2{}^{37}Cl$ $(M + 2)^+$ 234.0733, calcd for $C_{13}H_{13}N_2{}^{35}Cl$ (M^+) 232.0767, found 232.0754.

1,1-Dicyano-2-cyclohexyl-2-phenylethane (7a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44−7.29 (m, 5H), 4.18 (d, J = 5.5 Hz, 1H), 2.88 (dd, J = 9.8, 5.5 Hz, 1H), 2.05−0.78 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.76, 129.15, 128.75, 128.33, 112.22, 111.96, 52.30, 39.18, 31.12, 30.48, 27.02, 25.75, 25.63.

1,1-Dicyano-2-cyclohexyl-2-(4-methoxyphenyl)-ethane (7b). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.17 (d, J = 5.4 Hz, 1H), 3.81 (s, 3H), 2.84 (dd, J = 9.7, 5.4 Hz, 1H), 2.04−0.75 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.76, 129.40, 128.57, 114.40, 112.40, 112.00, 55.15, 51.51, 39.15, 31.06, 30.42, 27.21, 25.72, 25.67, 25.60; MS *m*/*z* (relative intensity) 268 (M^+, 34), 203 (94), 185 (13), 159 (27), 122(24), 121 (100), 122 (24), 115 (12), 91 (11), 55 (17); HRMS *m*/*z* calcd for $C_{17}H_{20}N_2O$ 268.1576, found 268.1571.

1,1-Dicyano-2-cyclohexyl-2-(4-chlorophenyl)ethane (7c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.19 (d, J = 5.4 Hz, 1H), 2.86 (dd, J = 9.8, 5.4 Hz, 1H), 2.20−0.75 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.06, 134.65, 129.63, 129.30, 112.03, 111.62, 51.61, 39.07, 30.98, 30.51, 26.92, 25.69, 25.66, 25.58.

1,1-Dicyano-3,3-dimethyl-2-phenylbutane (8a). The spectral data for this compound are consistent with the literature data:[39b] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (s, 5H), 4.23 (d, J = 5.6 Hz, 1H), 3.01 (d, J = 5.6 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ136.29, 129.28, 128.65, 128.53, 113.26, 113.17, 56.53, 34.76, 28.27, 24.88; MS *m*/*z* (relative intensity) 212 (M^+, 35), 197 (19), 156 (8), 147 (57), 132 (31), 105 (34), 91 (51), 77 (11), 57 (100); HRMS *m*/*z* calcd for $C_{14}H_{15}N_2Cl$ (M^+) 212.1313, found 212.1311.

1,1-Dicyano-3,3-dimethyl-2-(4-methoxyphenyl)butane (8b). The spectra data for this compound are consistent with the literature data:[50] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.2 (d, J = 5.6 Hz, 1H), 3.82 (s, 3H), 2.97 (d, J = 5.6 Hz, 1H), 1.09 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.61, 130.42, 128.24, 113.99, 113.31, 113.25, 55.99, 55.12, 34.90, 28.28, 25.10.

1,1-Dicyano-3,3-dimethyl-2-(4-chlorophenyl)butane (8c). The spectra data for this compound are consistent with the literature data:[50] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37−7.36 (m, 4H), 4.22 (d, J = 5.4 Hz, 1H), 2.99 (d, J = 5.4 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.81, 134.67, 130.68, 129.04, 112.97, 112.85, 56.15, 34.87, 28.30, 24.82; MS *m*/*z* (relative intensity) 248 ($(M + 2)^+$, 5) 246 (M^+, 14), 181 (76), 166 (31), 139 (24), 125 (37), 115 (24), 107 (11), 57 (100); HRMS *m*/*z* calcd for $C_{14}H_{15}N_2{}^{37}Cl$ $(M + 2)^+$ 248.0894, found 248.0892, calcd for $C_{14}H_{15}N_2{}^{35}Cl$ (M^+) 246.0924, found 246.0919.

Typical Procedures for the Synthesis of 6, 7, or 8 from the Reaction of 1-Aryl-2,2-dicyanoethenes 1a−c, Alkyl Iodide 3, 4, or 5, and 2b in Dry Ether Solution in the Presence of the Benzoyl Peroxide (Eq 2 and Table 2). About 6 mL of 15% triethylaluminum in hexane (5.4 equiv) was slowly added by a syringe three times (2 mL × 3) to a stirred solution which contained 1 mmol of 1-aryl-2,2-dicyanoethene **1a**, **1b**, or **1c**, 2 mmol of benzoyl peroxide, and 10−15 mmol of an alkyl iodide RI such as **3**, **4**, or **5** in dry diethyl ether (10 mL) at 0 °C over a period of 30 min. The stirred solution was then stirred at room temperature for a further 0.5−1 h, and the reaction was checked by TLC continuously until all the starting material disappeared. After the reaction was quenched by slowly pouring the solution into an ice-cold diluted hydrochloric acid aqueous solution, the product was extracted with dichloromethane. The yield was measured by ^{1}H NMR, and medium to high (77−100%) yields of the product **6**, **7**, or **8** were observed, which also could be easily purified by flash column chromatography. All spectral data of the final products are consistent with those shown in Table 1.

Typical Procedures for the Synthesis of 10, 11, or 12 from the Reaction of 9, Alkyl Iodide 3, 4, or 5, and 2a in THF Solution in the Presence of the Oxygen in the Air (Eq 3 and Table 3). These procedures are similar to the synthesis of **6**, **7**, and **8** except the amount of triethylborane was increased to 8−10 equiv and the reaction time was increased to 4−5 h.

Typical Procedures for the Synthesis of 10, 11, or 12 from the Reaction of 9, Alkyl Iodide 3, 4, or 5, and 2b in Dry Ether Solution in the Presence of Benzoyl Peroxide (Eq 4 and Table 4). These procedures are similar to those used for the preparation of alkanes **6**, **7**, and **8** as described above.

2-(2-Methyl-1-phenyl)propylmalonic Acid Dimethyl Ester (10). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27−7.12 (m, 5H), 3.99 (d, J = 11.2 Hz, 1H), 3.77 (s, 3H), 3.40 (s, 3H), 3.38 (dd, J = 11.2, 5.0 Hz, 1H), 2.04−1.92 (m, 1H), 0.84 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.23, 168.46, 138.25, 129.41, 127.78, 116.80, 55.56, 52.53, 52.10, 51.15, 30.27, 21.39, 17.65; MS *m*/*z* (relative intensity) 264 (M^+, 2), 222 (6), 201 (14), 189 (9), 163 (14), 162 (61), 132 (100), 121 (50), 103 (13), 91 (18), 77 (8), 59 (3); HRMS *m*/*z* calcd for $C_{15}H_{20}O_4$ 264.13616, found 264.13605.

2-(2-Methyl-1-phenyl)propyl-2-isopropylmalonic Acid Dimethyl Ester (10a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26−7.17 (m, 5H), 3.82 (s, 3H), 3.78 (s, 3H), 3.47 (d, J = 5.4 Hz, 1H), 2.16−2.04 (m, 1H), 2.04−1.92 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H),

(49) Campaigne, E.; Roelofse, W. L. *J. Org. Chem.* **1965**, *30*, 396.
(50) Mitchell, T. N. *J. Organomet. Chem.* **1974**, *71*, 27.

0.49 (d, J = 6.8 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.81, 171.16, 138.49, 130.80, 127.55, 126.57, 64.91, 54.88, 51.66, 51.57, 31.73, 31.07, 23.35, 20.82, 19.76, 17.39; MS m/z (relative intensity) 306 (M^+, 1), 243 (3), 231 (13), 221 (34), 189 (100), 174 (60), 159 (47), 121 (59), 91 (36), 59 (6); HRMS m/z calcd for $C_{18}H_{26}O_4$ 306.18311, found 306.18288.

2-(Cyclohexylphenyl)methylmalonic Acid Dimethyl Ester (11). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27−7.11 (m, 5H), 4.01 (d, J = 11.0 Hz, 1H), 3.77 (s, 3H), 3.39 (s, 3H), 3.36 (dd, J = 14.0, 5.0 Hz, 1H), 1.74−0.68 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.23, 168.49, 138.95, 129.25, 127.72, 126.69, 54.99, 52.47, 52.03, 51.00, 40.74, 31.80, 28.34, 26.45, 26.28, 26.02; MS m/z (relative intensity) 304 (M^+, 11), 271 (11), 254 (22), 244 (16), 222 (30), 200 (10), 172 (100), 162 (62), 148 (6), 105 (8); HRMS m/z calcd for $C_{18}H_{26}O_4$ 304.16746, found 304.16741.

2-(2,2-Dimethyl-1-phenyl)propylmalonic Acid Dimethyl Ester (12). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24−7.12 (m, 5H), 4.03 (d, J = 11.0 Hz, 1H), 3.76 (s, 3H), 3.47 (d, J = 11.0 Hz, 1H), 3.24 (s, 3H), 0.89 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.98, 168.63, 140.01, 129.91 (br), 127.43, 126.57, 55.23, 54.64, 52.68, 52.00, 34.26, 28.07; MS m/z (relative intensity) 278 (M^+, 2), 263 (4), 245 (2), 222 (100), 215 (7), 190 (11), 172 (6), 163 (24), 162 (92), 131 (7), 121 (3), 57 (1); HRMS m/z calcd for $C_{16}H_{22}O_4$ 278.15181, found 278.15227.

Typical Procedures for the Synthesis of 14, 15, or 16 from the Reaction of 13, Alkyl Iodide 3, 4, or 5, and 2b in Dry Ether Solution in the Presence of Benzoyl Peroxide (Eq 5 and Table 5). These procedures are similar to those used for the synthesis of **6**, **7**, and **8** which is shown in eq 2 and Table 2, except the reactions were carried out at room temperature for 4−5 h and a larger amount of triethylaluminum (about 8−10 equiv) was added to the solution.

3-(1-Phenyl-2-methylpropyl)pentane-2,4-dione (14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.05 (m, 5H), 4.43 (d, J = 12.0 Hz, 1H), 3.53 (dd, J = 12.0, 4.0 Hz, 1H), 2.29 (s, 3H), 1.82 (s, 3H), 081 (d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.62, 203.32, 137.79, 129.54, 128.02, 126.86, 73.69, 50.75, 30.61, 30.05, 28.33, 21.77, 17.21; MS m/z (relative intensity) 232 (M^+, 2), 231 (10), 229 (43), 227, (16), 201 (13), 189 (50), 175 (12), 173 (15), 171 (20), 159 (15), 157 (10), 148 (13), 147 (100), 145 (16), 143(18), 132 (27), 131 (34), 129 (32), 128 (18), 117 (21), 115 (13), 105 (23), 103 (13), 91 (35), 77 (11); HRMS m/z calcd for $C_{15}H_{20}O_2$ 232.1536, found 232.1456.

2,4-DNP Derivative of 3-(1-Phenyl-2-methylpropyl)-pentane-2,4-dione (14a). The color of this derivative is orange-yellow, and the mp is 228−232 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.20 (s, 1H), 10.81 (s, 1H), 9.16 (d, J = 2.8 Hz, 1H), 9.06 (d, J = 2.8 Hz, 1H), 8.42 (dd, J = 9.5, 2.4 Hz, 1H), 8.33 (dd, J = 9.5, 2.4 Hz, 1H), 8.07 (d, J = 9.5 Hz, 1H), 7.79 (d, J = 9.5 Hz, 1H), 7.30−7.16 (m, 5H), 4.23 (d, J = 12.1 Hz, 1H), 3.59 (dd, J = 12.1, 3.4 Hz, 1H), 2.20 (s, 3H), 1.86 (s, 3H), 0.87 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.70, 144.99, 144.85, 138.22, 138.08, 137.98, 130.24, 129.94, 129.78, 129.54, 129.25, 128.45, 127.81, 126.69, 123.38, 123.28, 116.31, 59.29, 50.07, 31.42, 29.63, 22.05, 16.30, 15.09, 14.10.

3-(Phenylcyclohexylmethyl)pentane-2,4-dione (15). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31−7.06 (m, 5H), 4.46 (d, J = 12.0 Hz, 1H), 3.51 (dd, J = 12.0, 4.5 Hz, 1H), 2.29 (s, 3H), 1.81 (s, 3H), 1.78−0.63 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.85, 203.66, 138.72, 129.47, 128.09, 126.86, 73.21, 50.77, 41.27, 32.32, 30.16, 28.22, 28.10, 26.48, 26.30, 26.00; MS m/z (relative intensity) 273 ((M + 1)$^+$, 3), 254 (4), 229 (74), 211 (26), 189 (4), 174 (8), 172 (81), 147 (100), 129 (51), 103 (17), 91 (38), 77 (13), 67 (4), 55 (27); HRMS m/z calcd for $C_{18}H_{24}O_2$ 272.1802, found 278.1767.

3-(2,2-Dimethyl-1-phenylpropyl)pentane-2,4-dione (16). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.18 (m, 5H), 4.44 (d, J = 11.0 Hz, 1H), 3.62 (d, J = 11.0 Hz, 1H), 2.33 (s, 3H), 1.55 (s, 3H), 0.82 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.07, 203.88, 139.84, 127.81, 126.72, 73.94, 54.19, 34.74, 30.49, 28.42, 26.73; MS m/z (relative intensity) 247 ((M + 1)$^+$, 3), 203 (8), 190 (56), 171 (6), 147 (100), 129 (63), 128 (20), 103 (34), 91 (22), 57 (66); HRMS m/z calcd for $C_{18}H_{24}O_2$ 246.1619, found 246.1632.

2,4-DNP Derivative of 3-(2,2-Dimethyl-1-phenylpropyl)pentane-2,4-dione (16a). The color of this derivative is orange-yellow, and it decomposes at 151−154 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 10.70 (s, 1H), 9.14 (d, J = 2.5 Hz, 1H), 9.06 (d, J = 2.5 Hz, 1H), 8.43 (dd, J = 9.5, 2.5 Hz, 1H), 8.36 (dd, J = 9.5, 2.4 Hz, 1H), 807 (d, J = 9.5 Hz, 1H), 7.96 (d, J = 9.5 Hz, 1H), 7.40−7.20 (m, 5H), 4.21 (d, J = 11.0 Hz, 1H), 3.68 (d, J = 11.0 Hz, 1H), 2.25 (s, 3H), 1.57 (s, 3H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.81, 155.26, 144.94, 144.75, 140.74, 138.26, 138.02, 130.35, 130.01, 129.59, 129.30, 127.57, 126.60, 123.47, 123.37, 116.20, 116.04, 58.81, 54.98, 34.92, 29.04, 16.21, 14.69.

Typical Procedures for the Synthesis of 18, 19, or 20 from the Reaction of 2-Cyclohexen-1-one (17), Alkyl Iodide 3, 4, or 5, and 2a in THF Solution in the Presence of the Oxygen in the Air (Eq 6 and Table 6). These procedures are similar to those used for the synthesis of alkenes **6**, **7**, and **8**, except the amount of triethylborane was increased to 8−10 equiv and the reaction time was increased to 4−5 h.

Typical Procedures for the Synthesis of 18, 19, or 20 from the Reaction of 17, Alkyl Iodide 3, 4, or 5, and 2b in Dry Ether Solution in the Presence of Benzoyl Peroxide (Eq 7 and Table 7). These procedures are similar to those used for the synthesis of **6**, **7**, and **8**.

3-Isopropylcyclohexanone (18). The spectral data for this compound are consistent with the literature data:[41d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50−1.20 (m, 10H), 0.91 (d, J = 6.4 Hz, 3H), 0.90 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.57, 45.42, 45.33, 41.49, 32.49, 28.34, 25.52, 19.54, 19.31.

3-Cyclohexylcyclohexanone (19). The spectral data for this compound are consistent with the literature data:[51] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50−0.82 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.57, 45.46, 44.56, 42.57, 41.49, 29.86, 29.76, 28.33, 26.49, 26.47, 26.43, 25.52.

3-*tert*-Butylcyclohexanone (20). The spectral data for this compound are consistent with the literature data:[41d] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50−1.20 (m, 9H), 0.90 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.77, 49.24, 43.51, 41.19, 32.58, 27.04, 26.02, 25.54.

21a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87−3.79 (m, 1H), 3.79−3.68 (m, 1H), 3.66−3.60 (m, 1H), 2.50−1.40 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.22, 82.35, 67.90, 44.67, 44.11, 41.43, 29.12, 27.65, 25.77, 24.94; MS m/z (relative intensity) 168 (M^+, 2), 122 (1), 111 (1), 110 (9), 105 (1), 98 (4), 97 (7), 96 (3), 85 (7), 83 (2), 81 (2), 79(2), 77 (2), 72 (4), 70 (100), 69 (4); HRMS m/z calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1170.

21b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85−3.60 (m, 3H), 2.60−1.42 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.67, 82.36, 68.07, 43.73, 43.64, 41.39, 29.06, 28.25, 25.85, 25.15; MS m/z (relative intensity) 168 (M^+, 2), 149 (7), 141 (12), 129 (5), 110 (11), 97 (26), 85 (17), 83 (12), 81 (8), 77 (18), 70 (100), 69 (15); HRMS m/z calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1173.

Acknowledgment. Financial support of this work by the National Science Council of the Republic of China is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C spectra of compounds **1a**−**c**, **6a**−**c**, **7a**−**c**, **8a**−**c**, **9**, **10**, **10a**, **11**−**14**, **14a**, **15**, **16**, **16a**, **18**−**20**, and **21a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020681B

(51) Rieke, R. D.; Klein, W. R.; Wu, T.-C. *J. Org. Chem.* **1993**, *58*, 2492.