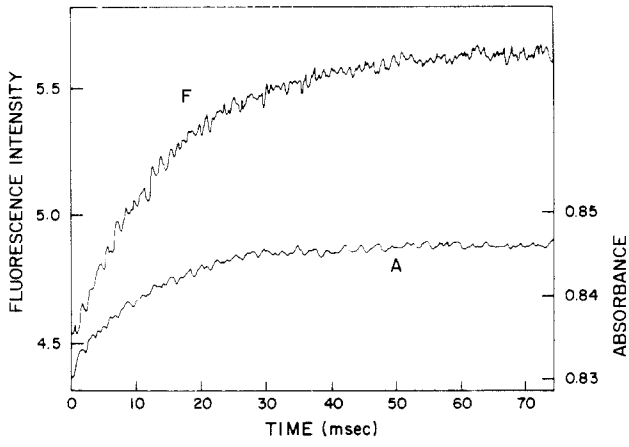

Figure 1. Kinetics of ADLAA binding to vancomycin. Recording of total fluorescence intensity beyond 400 nm (F) on mixing ADLAA and vancomycin (final concentrations 1.0 μM and 10.0 μM, respectively) in 0.1 M phosphate buffer, pH 7.0. Also shown is a recording of the absorbance at 550 nm (A) on mixing ADLAA and vancomycin (final concentrations 10.0 μM each) in a solution containing 33 μM phenol red at pH 7.6.

undergoes fluorescence enhancement on binding to these antibiotics. ADLAA was mixed in a stopped-flow spectrophotometer with a series of vancomycin solutions and the change in fluorescence[7] monitored. In all cases, monotonic increases were observed (Figure 1) which could be fitted[9] to a single-step binding process (eq 1, where D is ADLAA and V is vancomycin). This

$$D + V \underset{}{\overset{K_1(=k_1/k_{-1})}{\rightleftharpoons}} DV \qquad (1)$$

procedure yielded $k_1 = (9.3 \pm 1.6) \times 10^6$ s^{-1} M^{-1} and $k_{-1}(=k_1/K_1) = 31 \pm 5$ s^{-1}. Since the value of k_1 did not vary systematically over the concentration range employed,[7] the binding reaction is, kinetically, a bimolecular process under these conditions.

Similar results were obtained for ristocetin and α-avoparcin, leading to rate constants for binding (k_1) of $(7.2 \pm 2.1) \times 10^6$ and $(4.1 \pm 1.3) \times 10^6$ s^{-1} M^{-1}, respectively, and dissociation (k_{-1}) of (24 ± 7) s^{-1} and (28 ± 9) s^{-1}, respectively.

These results suggest that the same or a similar process is rate-determining in all three cases. That this slow step is not rearrangement of the dansyl group in a rapidly formed initial complex was demonstrated by the employment of a complementary measurement of the rates. At a pH above the pK_a of the N-terminal ammonium group, peptide binding is accompanied by proton uptake,[12] which can be followed by changes in the absorbance of phenol red at 550 nm,[13] as also shown in Figure 1. These data yielded the same rate constants within the experimental uncertainty limits, as did the fluorescence data, for the binding of ADLAA to both vancomycin and ristocetin, and similar rate constants were obtained for *N,N'*-diacetyl-L-lysyl-D-alanyl-D-alanine. Thus the rate-determining step in the binding of ADLAA does not involve the dansyl group but is apparently characteristic of specific binding of a L-lysyl-D-alanyl-D-alanine peptide. Since the step is common to the three antibiotics it cannot involve in any way the conformational change of the N-terminus specific to vancomycin.

The magnitude of the rate constant k_1 is remarkably, and probably impossibly, small for a diffusion-controlled combination of molecules of the size of ADLAA and the antibiotics.[14] Experiments in glycerol solutions bear this out—the rate constant k_1 of vancomycin is not affected by viscosity.[15] Hence a two-(at least) step binding process must obtain, where the first step involves diffusion-controlled formation of a weakly bound initial complex, which then rearranges in a slower step. The slow step might entail a common conformational change or perhaps a desolvation process.[16] We are looking into these possibilities.[17]

Acknowledgment. We are grateful to Wesleyan University for financial assistance.

(6) Popieniek, P. H.; Pratt, R. F. *Anal. Biochem.* **1987**, *165*, 108-113.
(7) Experiments with vancomycin were carried out in 0.1 M phosphate buffer at pH 7.0 and 25 °C. The stopped-flow system has been described previously.[8] The excitation wavelength was 330 nm, and total emission beyond 400 nm was monitored. The concentration of ADLAA was 1.0 μM, and the concentration of vancomycin was varied from 1.0 to 30.0 μM. Experiments with ristocetin and avoparcin A were performed similarly but at pH 6.5 and 6.0, respectively. Vancomycin B, ristocetin A, and α-avoparcin were generous gifts from Eli Lilly and Co., H. Lundbeck A/S, and American Cyanamid Co., Lederle Laboratories, respectively.
(8) Anderson, E. G.; Pratt, R. F. *J. Biol. Chem.* **1981**, *256*, 11401-11404.
(9) Measurements of fluorescence as a function of time were fitted by means of a nonlinear least-squares procedure[10] and an integrated rate equation.[11] Values for the equilibrium constants, K_1, were taken from fluorimetric titrations.[6]
(10) Johnson, M. L.; Halvorson, H. R.; Ackers, G. K. *Biochemistry* **1976**, *15*, 5363-5371.
(11) Rorabacher, D. B.; Turan, T. S.; Defever, J. A.; Nickels, W. G. *Inorg. Chem.* **1969**, *8*, 1498-1506.
(12) Brown, J. P.; Feeney, J.; Burgen, A. S. V. *Mol. Pharmacol.* **1975**, 11, 119-125.
(13) Reacting solutions at 25 °C contained 10.0 μM each of ADLAA and vancomycin or ristocetin, 33.0 μM phenol red, and 0.2 M potassium chloride and were adjusted to pH 7.6 after purging with nitrogen.
(14) Berg, O. G.; von Hippel, P. H. *Ann. Rev. Biophys. Biophys. Chem.* **1985**, 14, 131-160.
(15) Measurements of the equilibrium and rate constants of binding of ADLAA to vancomycin were made fluorimetrically as described above. The buffers included 30% and 60% (w/v) glycerol on one hand and, to give solutions of essentially unchanged (with respect to the aqueous conditions) viscosity but equivalent (to the glycerol solutions) dielectric constants, 15% and 30% (w/v) ethanol on the other. Both binding strength and rates were decreased but to the same extents, within experimental uncertainty, in the glycerol solutions as in the ethanol.
(16) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039-1057.
(17) We do not understand the disparity between our results and those of Williamson et al.[4a] with respect to vancomycin. The aggregation of vancomycin and its peptide complex at the concentrations used (6 mM)[18] may have produced complications; however, spurred by a reviewer and an editor we undertook some 400 MHz ^{1}H NMR measurements (^2H_2O, 20 mM phosphate buffer, pD 6.5, 6 mM vancomycin or ristocetin, 12 mM *N,N'*-diacetyl-L-lysyl-D-alanyl-D-alanine) which showed the methyl group of the C-terminal D-alanine of the peptide to be in slow exchange at 60° in both the vancomycin and ristocetin complexes; the vancomycin observation is contrary to that of Williamson et al.[4a] but consistent with our fluorescence data.
(18) Nieto, M.; Perkins, H. R. *Biochem. J.* **1971**, *123*, 773-787.

Nickel(0)-Promoted Cyclization of Enynes with Isocyanides: A New Route to Polycyclic Cyclopentenone Skeletons

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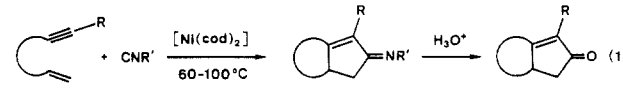
We report herein the first successful case of nickel(0)-promoted cyclization of enynes and isocyanides to form 1-imino-2-cyclopentenes which may be hydrolyzed to the corresponding cyclopentenones, as shown in eq 1.

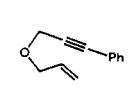
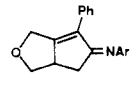
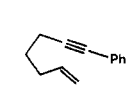
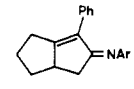
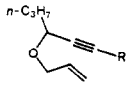
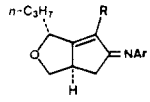
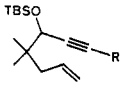
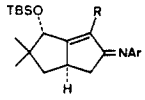
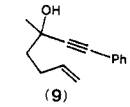
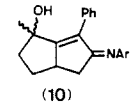
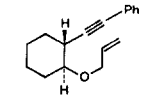
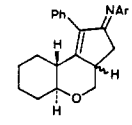


Much interest has recently been directed toward transition-metal-promoted synthesis of cyclopentanoids from alkenes, alkynes, or enynes, and carbon monoxide.[1,2] Of these reactions, however,

(1) Reviews: (a) Zirconium: Negishi, E.-I. *Acc. Chem. Res.* **1987**, *20*, 65. (b) Cobalt: Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (c) Nickel and palladium: Chiusoli, G. P. *J. Organomet. Chem.* **1986**, *300*, 57.

0002-7863/88/1510-1286$01.50/0

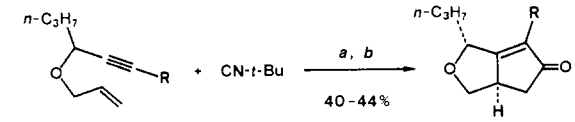
Table I. Reaction of Enynes with 2,6-Dimethylphenyl Isocyanide in the Presence of $[Ni(cod)_2]$ and n-Bu_3P[a]

entry	enyne	solvent, temp (°C), time (h)[b]	product[c] (major isomer)	yield, %[d] (isomer ratio)[e]
1	 (1)	DMF, 60, 12	 (2)	62
2	 (3)	DMF, 100, 12	 (4)	29
3	 (5a) R = Ph	DMF, 60, 10	 (6a) R = Ph	92 (2:1)
4		$PhCH_3$, 60, 6		84 (2:1)
5		THF, 60, 6		80 (2:1)
6	(5b) R = n-C_4H_9	DMF, 60, 12	(6b) R = n-C_4H_9	47[f] (3:1)
7	 (7a) R = Ph	DMF, 100, 12	 (8a) R = Ph	83 (10:1)
8		$PhCH_3$, 100, 10		72 (8:1)
9	(7b) R = n-C_4H_9	DMF, 100, 12	(8b) R = n-C_4H_9	50 (17:1)
10	 (9)	DMF, 100, 12	 (10)	39 (2:1)[g]
11	 (11)	DMF, 100, 5	 (12)	37[h]

[a] Carried out under nitrogen on a 1 mmol scale in the ratio of enyne/ArNC/$[Ni(cod)_2]$/n-Bu_3P = 1:2:1:2, unless otherwise stated. [b] Under the given condition, the starting material, enyne, had been completely consumed. [c] Ar = 2,6-dimethylphenyl. [d] Yields of pure products isolated by column chromatography. [e] Determined by 400-MHz ^1H NMR. [f] In the presence of 3 equiv of n-Bu_3P. [g] Stereochemical assignment has not yet been achieved. [h] A single isomer of unknown stereochemistry at the bridgehead.

formation of cyclopentenone skeletons has so far been restricted to only three metals, namely, titanium-,[2c] zirconium-,[2f,g] or cobalt-promoted[2k-q] cyclization of enynes with carbon monoxide. Our new process has been achieved by nickel(0) complexes in combination with an isocyanide[3] as an isoelectronic counterpart of carbon monoxide.[4]

Scheme I[a]



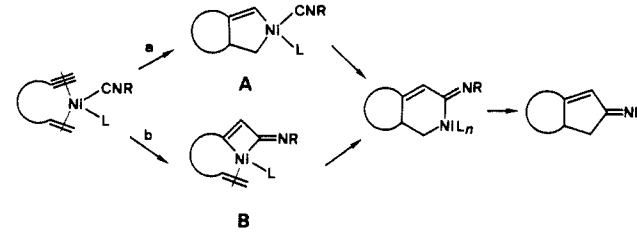
5a or 5b

13a, R = Ph (4:1)

13b, R = n-C_4H_9 (4:1)

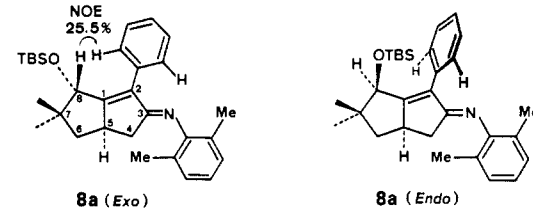
[a] (a) t-BuNC (2 equiv), $[Ni(cod)_2]$ (1 equiv), R_3P (2 equiv), benzene or toluene, 60–80 °C, 12 h. (b) CSA (1 equiv), THF/H_2O (5:1), room temperature, 17 h.

Scheme II



When a mixture of a 1,6-enyne, 2,6-dimethylphenyl isocyanide (2 equiv), tri-n-butylphosphine (2 equiv), and bis(1,5-cyclooctadiene)nickel(0), $[Ni(cod)_2]$ (1 equiv), was heated in DMF under nitrogen at 60–100 °C for 6–12 h, the corresponding 3-iminobicyclo[3.3.0]oct-1-ene derivative was obtained in high yields after column chromatography.[5] Several representative results obtained under this standard condition are summarized in Table I.

The following features deserve comment. (1) Oxygen functionalities between the two unsaturated bonds appeared to facilitate the cyclization. Thus, in contrast to the high reactivity of **1**, the carbon analogue **3** reacted only at 100 °C to form **4** in lower yields (entry 2). A free alcohol did not largely disturb the reaction (entry 10). (2) Aromatic acetylenes exhibited higher reactivity and afforded higher yields than aliphatic acetylenes (**5a** versus **5b** and **7a** versus **7b**).[6] (3) Since **2** and **4** were obtained as a single isomer, the stereochemistry of the imino group may be fixed to be anti with respect to the C(2) substituent owing to the steric repulsion. (4) A considerable 1,3-stereoselection has been observed in **6** and **8**. The major isomer of **8a** has been characterized to be C(8)-exo,



8a (*Exo*) **8a** (*Endo*)

based on the NOE analysis. Thus, as shown below, the major isomer showed a large NOE (25.5%) between the C(8) nearly-in-plane hydrogen and the ortho hydrogens of the phenyl group

(2) Representative examples are as follows. Titanium: (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (b) Grubbs, R. H.; Miyashita, A. *J. Chem. Soc., Chem. Commun.* **1977**, 864. (c) Parshall, G. W.; Nugent, W. A.; Chan, D. M.-T.; Tam, W. *Pure Appl. Chem.* **1985**, *57*, 1809. Zirconium: (d) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (e) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470. (f) Negishi, E.-I.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (g) Negishi, E.-I.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (h) Buchwald, S. L.; Watson, B.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. Cobalt: (i) Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560. (j) Billington, D. C. *Tetrahedron Lett.* **1983**, *24*, 2905. (k) Shore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. (l) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. (m) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041. (n) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851. (o) Smit, W. A.; Gybin, A. S.; Shashkov, E. D.; Strychkov, Y. T.; Kyz'mina, L. G.; Mikaelian, G. S.; Caple, R.; Swanson, E. D. *Tetrahedon Lett.* **1986**, *27*, 1241. (p) Simanian, S. O.; Smit, W. A.; Gybin, A. S.; Shashkov, A. S.; Mikaelian, G. S.; Tarasov, V. A.; Ibragimov, I. I.; Caple, R.; Froen, D. E. *Tetrahedron Lett.* **1986**, *27*, 1245. (q) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128. Nickel: (r) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418.

(3) Nickel–isocyanide complexes have been extensively studied by Otsuka and his co-workers. (a) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994. (b) Otsuka, S.; Yoshida, T.; Tatsuno, Y. *J. Am. Chem. Soc.* **1971**, *93*, 6462. (c) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180.

(4) No reaction occurred under CO atmosphere. In the course of our present study, Trost reported a 1,3-diene synthesis from enynes catalyzed by nickel–chromium systems: Trost, B. M; Tour, M. *J. Am. Chem. Soc.* **1987**, *109*, 5268.

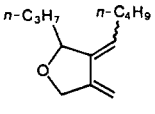
(5) All products showed consistent spectral data and elemental analysis and/or high resolution mass data (see Supplementary Material).

(6) A silylacetylene (**5**, R = $SiMe_3$) was recovered unchanged, while a terminal acetylene (**5**, R = H) and an acetylenecarboxylate (**5**, R = COOMe) formed a complex mixture of product. It may be noted that the zirconium-promoted reaction has been applied only to silylacetylenes, while the cobalt-promoted one seems to be applicable to almost all types.

on C(2), while little effect has been observed with the minor isomer, in which the bulky endo siloxy group might prevent rotation of the phenyl group. The stereochemistry of other products, **6a**, **6b**, and **8b**, has been assigned by spectral comparison with **8a**.[7] It should be mentioned here that the preference of the C(8)-exo isomer is the same as the stereoselection observed in the cobalt-promoted cyclization.[2l,n] Higher stereoselections have been attained with alkylacetylenes than with phenylacetylenes (**6a** versus **6b** and **8a** versus **8b**). The stereoselection did not depend on the solvent polarity (entries 3-5, 7, and 8). (5) A six-membered ring was also formed from a 1,7-enyne system (entry 11), tricyclic product (**12**) being formed as a single stereoisomer.[8]

tert-Butyl isocyanide could be used in place of 2,6-dimethylphenyl isocyanide. The primary products, cyclic imines, were directly hydrolyzed [CSA (1 equiv), THF/H_2O (5:1), room temperature, 17 h] to the corresponding ketones in approximately 40% overall yields, as shown in Scheme I. The stereoselectivities were similar to those observed with the aromatic isocyanide. Ketones **13** were also obtained by acidic hydrolysis of **6** under similar conditions in about 50% yield.

Although the mechanism has not yet been clarified, at least two possible mechanisms may be envisaged, as shown in Scheme II. One involves nickelacyclopentene intermediates (A)[9] which undergo insertion of isocyanide,[10] while the other proceeds through iminonickelacyclobutene intermediates (B)[11,12] prior to the participation of the olefin part. The cyclization was completely inhibited by a bidentate ligand such as $Ph_2P(CH_2)_3PPh_2$ and also sensitive to the nickel-to-isocyanide ratios; no cyclization products were obtained in the presence of 3 equiv of isocyanide although the starting enynes were consumed. Cyclic 1,3-dienes anticipated from Trost's recent study[4] were obtained as byproducts not from aromatic acetylenes but from aliphatic ones, e.g., **14** from **5b**,



14

especially in the absence of isocyanide. These observations might be pertinent to the elucidation of the mechanism, but we must wait for further studies to visualize the mechanism more clearly. The present reaction should be synthetically useful and may be added as a new member in a list of a variety of nickel-promoted carbon-carbon bond-forming reactions.[13]

Acknowledgment. We thank H. Fujita for measurements of 400-MHz NMR spectra.

Supplementary Material Available: A typical experimental procedure for the preparation of **6a** and spectral data for **2**, **4**, **6**, **8**, **10**, **12**, and **14** (4 pages). Ordering information is given on any current masthead page.

(7) In ^1H NMR spectra, the proton on C(8) appears at a higher field in exo isomers than in endo.

(8) The stereochemistry of **12** has not yet been determined, since the same stereoselection as other products may predict an α isomer at the newly formed bridgehead carbon and a boat form of the six-membered middle ring.

(9) Formation of nickelacyclopentanes[2r] and nickelacyclopentadienes from nickel(0) complexes with ethylene and acetylenes, respectively, has been reported. Eisch, J. J.; Damasevitz, G. A. *J. Organomet. Chem.* **1975**, *96*, C19.

(10) A closely related reaction is the formation of cyclic imines from bis(π-allyl)nickels and an isocyanide: Baker, R.; Cookson, R. C.; Vinson, J. R. *J. Chem. Soc., Chem. Commun.* **1974**, 515. Baker, R.; Copeland, A. H. *Tetrahedron Lett.* **1976**, 4535.

(11) Some bis(isocyanide)(acetylene)nickel(0) complexes have been isolated.[3b] Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* **1972**, *36*, 191. It has also been reported that the reaction of tetrakis(isocyanide)nickel(0) with diphenylacetylene affords diiminocyclobutenes: Suzuki, Y.; Takizawa, T. *J. Chem. Soc., Chem. Commun.* **1972**, 837.

(12) **Note Added in Proof.** Eisch and his co-workers reported several years ago nickel(0)-mediated reactions of diphenylacetylene with trimethylsilyl isocyanide and proposed an iminonickelacyclobutene intermediate: Eisch, J. J.; Aradi, A. A.; Han, K. I. *Tetrahedron Lett.* **1983**, *24*, 2073.

(13) Tamao, K.; Kumada, M. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley: Chichester, 1987; Vol. 4, pp 819-887. Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 613-797.

Regioselective Double Vicinal Carbon-Carbon Bond-Forming Reactions of Electron-Deficient Alkenes by Use of Allylic Stannanes and Organoiodo Compounds

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The introduction of two different carbon-functional groups into a carbon-carbon double bond of unsaturated molecules is of great value in organic synthesis. A number of approaches have been advanced to this problem for α,β-unsaturated ketone systems in recent years.[1] Most of these approaches involve the conjugated addition of a carbon nucleophile to the β-carbon of the enones, followed by trapping the enolate at the α-carbon with a carbon electrophile. However, such a three-component coupling reaction has been less well developed for the other unsaturated compounds.[2-5] We now report a novel type of double vicinal C-C bond-forming reactions on electron-deficient alkenes by use of allylic stannanes and organoiodo compounds.[6,7]

A benzene solution of 1,1-dicyano-2-phenylethene (**1a**, 1 mmol), allyltributylstannane (**2a**, 2 mmol), and methyl iodide (5 mmol) in the presence of azobis(isobutyronitrile) (AIBN, 0.2 mmol) was refluxed for 6 h under a nitrogen atmosphere[8] (see Scheme I). Workup of the reaction mixture by partition between acetonitrile and hexane followed by column chromatography on silica gel gave 4,4-dicyano-5-phenyl-1-hexene (**3a**) as a sole product in 85% yield. In a similar manner, 1,1-dicyano-2-(*p*-substituted phenyl)ethenes were converted into the corresponding 5-aryl-4,4-dicyano-1-hexene derivatives in good yields.[9] The electron-donating substituents on the phenyl ring of dicyanoethenes reduced the yields of products. The allyl function from allylstannane was regioselectively introduced into the α-carbon from the cyano group of the 1,1-dicyanoethenes and the methyl group from methyl iodide into the β-carbon.

Similarly a three component coupling reaction on 1,1-dicyano-2-phenylethene occurred by using a combination of allyl and 2-methyl-2-propenyltributylstannane[10] with a variety of organoiodo compounds such as alkyl, allyl, and benzyl iodides as well as iodobenzene. The reactivity of alkyl iodides decreased in the following order: primary > secondary > tertiary. Allyl bromide and chloride could be utilized for this coupling reaction

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(8) Benzoyl peroxide could also be utilized as a radical initiator, but it was less effective.

(9) All the new compounds obtained in this study showed satisfactory spectral data (^1H NMR, ^{13}C NMR, IR, and mass) and elemental analyses.

(10) When 3-methyl-2-butenyltributylstannane and benzyltributylstannane were used, no coupling products were obtained; cf. ref 7a.

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