Palladium-Catalyzed Propargylic vs. Allylic Alkylation

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The relative reactivities of allylic and propargylic acetates toward palladium(0)-catalyzed substitution by various nucleophiles were studied by using three types of model substrates: (a) monofunctional allylic and propargylic acetates with similar structural properties; (b) a bifunctional substrate containing both allyl and propargyl functionalities with no apparent interaction between them; (c) conjugated bifunctional systems, in which the two functionalities may interact with one another. Palladium(0)-catalyzed substitution of propargylic acetates by various carbon nucleophiles was found to be less general than the analogous substitution of allylic acetates. Three modes of reactivity were observed, corresponding to three groups of nucleophiles: (a) stabilized carbanions such as sodium dimethyl malonate, which do not react with propargylic acetates but react readily with allylic acetates; (b) nonstabilized organometallics such as phenylzinc chloride, which react with propargylic and allylic acetates at comparable rates (reaction with the former yielding the allenic product exclusively); and (c) allyl- and allenylstannanes, which react with allylic acetates but do not react with isolated propargylic acetates (except for special cases where the propargylic acetate is also an allylic one). Certain similarities between regioselectivity phenomena in organopalladium and organocopper chemistry are discussed.

Palladium(0)-catalyzed allylation[1] has become, within the past 2 decades, a versatile and widely used synthetic tool for highly controlled formation of carbon–carbon bonds.[1] This methodology enables chemoselective and stereospecific substitution of normally nonreactive allylic leaving groups (X) using a wide variety of carbon nucleophiles (Nu), ranging from stabilized carbanions to nonstabilized organometallics (Scheme I).

However, the propargylic electrophile, similar in chemical properties to its allylic counterpart, has not been widely applied to analogous palladium-mediated transformations. This is due to the expected linear geometry of the η^3-allenyl unit II (Scheme II) which renders it less favorable for bidentate binding to the transition metal.

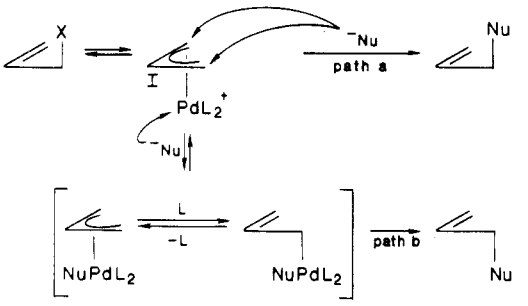
Such a consideration, however, should only apply to stabilized carbanion nucleophiles, such as the enolates of malonic esters, β-dicarbonyls, β-keto sulfones, etc., which directly attack the π-allyl ligand[2] (path a in Scheme I). However, nonstabilized nucleophilic organometallics such as methyl, allyl, vinyl, and aryl derivatives of tin[3], zinc,[4] aluminum,[5] and zirconium[5,6] react by a different mechanistic pathway, involving transmetalation followed by reductive elimination of two carbon ligands, as shown in path b in Scheme I. Consequently, propargylic substitution via this pathway should be as efficient as allylic substitution, if not more so. Indeed, a number of recently reported palladium-catalyzed cross-coupling reactions between propargylic electrophiles and nonstabilized organozinc or organomagnesium nucleophiles[7] indicate that propargylic heterosubstituents are useful substrates for Pd(0) chemistry.[8]

In this paper we report on a study of the relative reactivities of allylic and propargylic acetates toward palladium-catalyzed substitution by various nucleophiles.

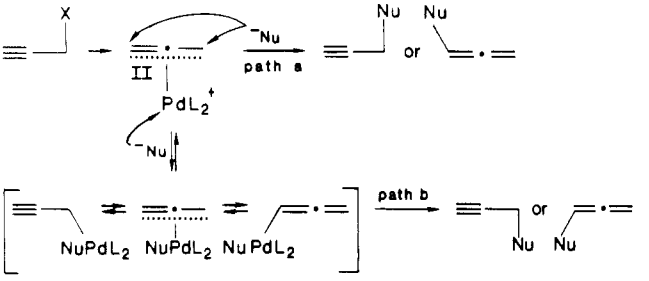
Results and Discussion

Using appropriate model substrates, reactivities of allylic and propargylic systems were compared. Thus, a number of allylic and propargylic acetates were prepared and allowed to react with a representative set of nucleophilic reagents in the presence of catalytic amounts of $Pd(PPh_3)_4$ in THF at room temperature. Three types of substrates were used: (a) monofunctional substrates having similar structural properties, such as **1** and **2** or **3** and **4**; (b) a nonconjugated bifunctional system (**5**) containing both allyl

Scheme I



Scheme II



† Incumbent of the Joseph and Madeleine Nash Career Development Chair established by Fondacion Madelon, Zurich, Switzerland.

(1) For reviews, see: (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Berlin, 1980. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (d) Trost B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 779.

(2) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215; *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(3) (a) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833. (b) Keinan, E.; Peretz, M. *J. Org. Chem.* **1983**, *48*, 5302.

(4) Matsushita, H.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 2882.

(5) (a) Matsushita, H.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1982**, 160. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

(6) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310.

(7) (a) Luong, T. J.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019. (b) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 1451. (c) Ruitenberg, K.; Kleijn, H.; Westmijze, J.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 405. (d) Kleijn, H.; Meijer, J.; Overbeek, G. C.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 97. (e) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103. (f) Elsevier, C. J.; Mooiweer, H. H.; Kleijn, H.; Vermeer, P. *Tetrahedron Lett.* **1984**, *25*, 5571. See also: (g) Colas, Y.; Cazes, B.; Gore, *J. Tetrahedron Lett.* **1984**, *25*, 845. (h) Yamada, Y.; Suzukamo, G.; Yoshioka, H.; Tamaru, Y.; Yoshida, Z. *Ibid.* **1984**, *25*, 3599.

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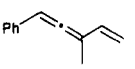
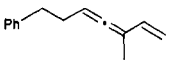
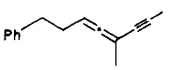
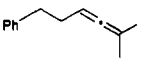
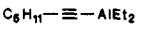
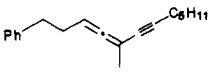
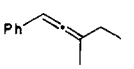
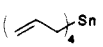
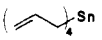
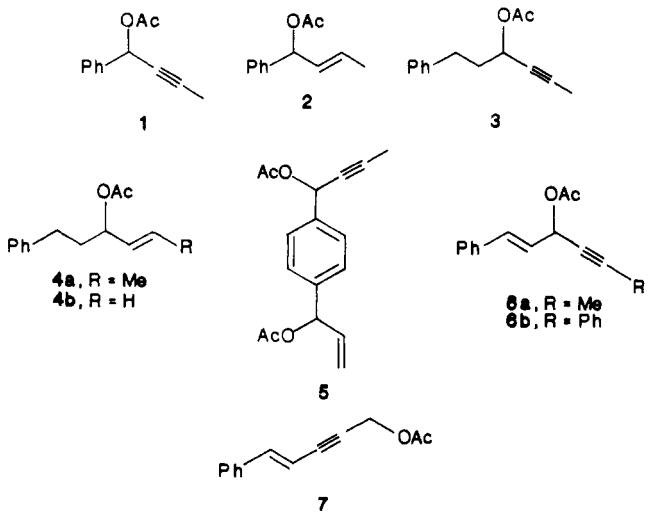
Table I. Palladium(0)-Catalyzed Propargylic Substitution[a]

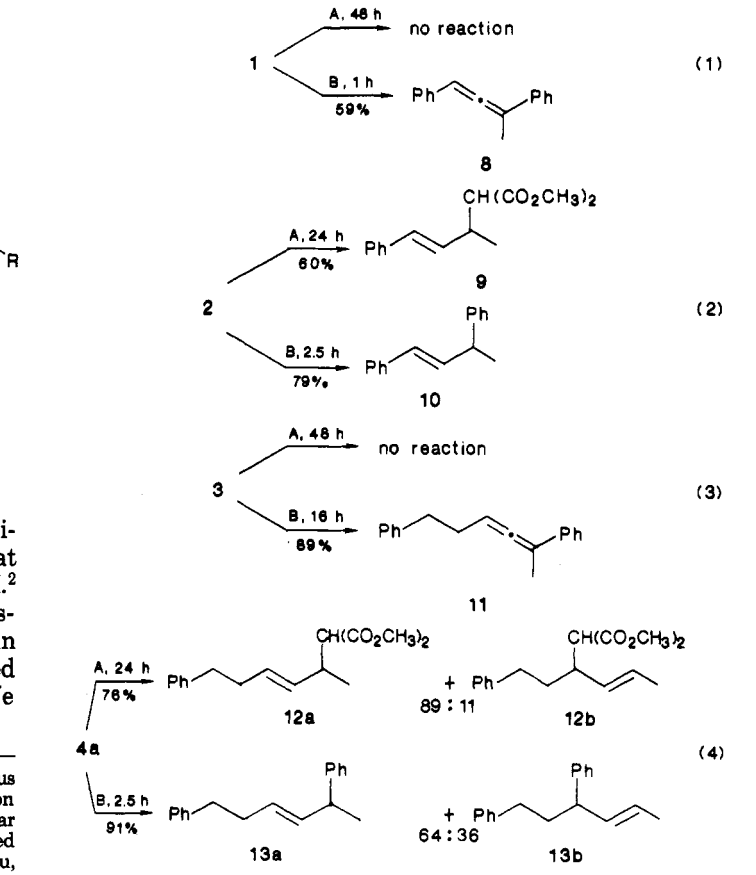
substrate	nucleophile	time (h)	product	yield (%)
1		0.8	 14	36
3		2	 15	68
3		96	 16	39
3	MeZnCl	40	 17	62
3		12	 18	87
1	Et_3Al	3	 19	68
1		48	no reaction	
3		72	no reaction	

[a] All reactions were carried out according to the general procedure given in the Experimental Section. Yields are of isolated products.

and propargyl functionalities with no apparent interaction between them; (c) conjugated bifunctional systems, **6** or **7**, in which the two functionalities may interact with one another.



A. Monofunctional Substrates. The enolate of dimethyl malonate is a typical stabilized nucleophile that reacts with π-allyl Pd complexes via path a in Scheme I.[2] On the other hand, phenylzinc chloride is a typical nonstabilized nucleophile reacting according to path b in Scheme I.[4] The two mechanistic alternatives are reflected by differing stereospecificities and regioselectivities.[9] We started our comparative study by reacting four simple monofunctional substrates **1**–**4** with 1.5 equiv of either sodium dimethyl malonate (A) or phenylzinc chloride (B) in the presence of 5–7 mol % $Pd(PPh_3)_4$ in THF at room temperature (eq 1–4).



It is clear that the two nucleophiles display distinct modes of reactivity not only with respect to allylic but also

(8) It has been recently shown by Tsuji and his co-workers that various propargylic carbonates undergo Pd(0)-catalyzed nucleophilic substitution by 1,3 dicarbonyl compounds at 60–80 °C. We did not observe similar transformations with our propargylic acetates when reactions were carried out at room temperature. Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196.

(9) (a) Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769. (b) Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648.

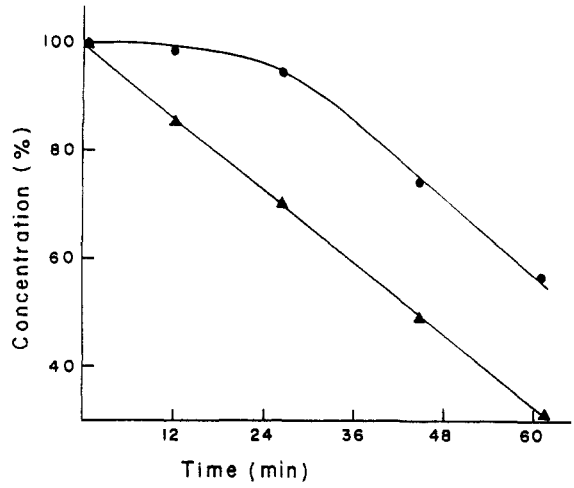


Figure 1. Pd(0)-catalyzed competitive substitution of 1 and 2 with PhZnCl: PhZnCl (1 mmol) was added to a 5-mL THF solution containing 1 and 2 (1 mmol each) and $Pd(PPh_3)_4$ (0.05 mmol) at room temperature. Disappearance of 1 (▲) and 2 (●) was detected by GC (10% SE-30 on Chromosorb W).

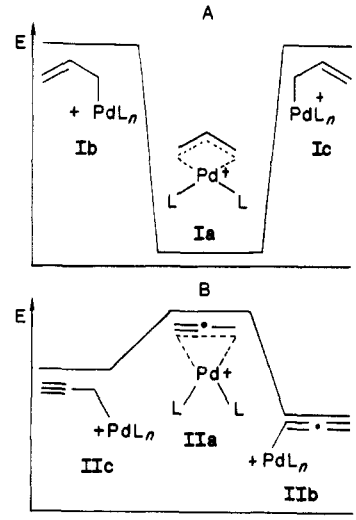
to propargylic substitution. Stabilized carbanions, for example, do not react with propargylic acetates 1 and 3[8] whereas the family of nonstabilized organometallics react rapidly with them, exhibiting highly regioselective formation of allenic products. Additional examples of this mode of reactivity for nonstabilized nucleophiles are given in Table I.

Interestingly, tetraallylstannane is completely inert with respect to propargylic acetates (Table I) but reacts with conjugated propargylic acetates (vide infra). This compound (as well as allenylstannane) is known to exhibit unique regioselectivity that differs from the characteristic behavior of both stabilized and nonstabilized nucleophiles.[9a]

With regard to the nonstabilized nucleophiles, it is desirable to determine the relative rates of reaction of the allylic and propargylic electrophiles. In order to check this point, three competition experiments were carried out by using equimolar mixtures of allylic and propargylic acetates. The first of these was performed with equimolar quantities of 1 and with 1 equiv of vinylzinc chloride. Both substrates were consumed at comparable rates except during a short latent period that was observed in the case of the allylic acetate (Figure 1). The source of this latency is at present unknown. In a second experiment, two other substrates, 3 and 4a, were compared. Behavior very similar to that shown in Figure 1 was observed in this case, namely, comparable reaction rates and a short latent period in the conversion of **4a**. A third experiment compared the relative reactivity of 3 and **4b** toward vinylzinc chloride. Here, consumption of allylic acetate **4b** was slightly faster than that of propargylic acetate 3, a situation that may be attributed to the smaller steric demands of **4b** relative to 3. These results indicate that both allylic and propargylic acetates, if similarly substituted, react with nonstabilized nucleophiles at comparable rates. Obviously, these rates should be influenced by the steric and electronic character of the allylic and propargylic substituents (vide infra, Scheme IV).

Both these results and literature reports of palladium-catalyzed propargylic substitutions[7] indicate that oxidative addition of both allylic and propargylic acetates to Pd(0) occur equally well. Thus, the observed differences in reactivity between these two functional groups toward various nucleophiles probably originates from the nature of the Pd(II) intermediate (I and II in Schemes I and II)

Scheme III. Hypothetical Relative Energies of Allyl Pd(II) (Scheme IIIA) and Propargyl Pd(II) Complexes (Scheme IIIB)



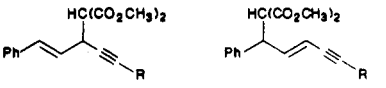
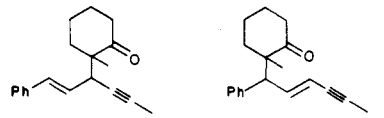
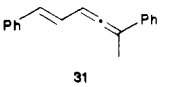
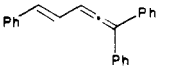
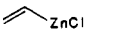
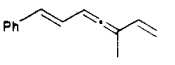
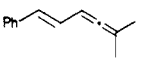
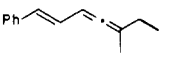
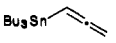
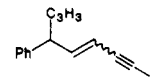
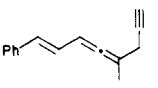
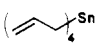
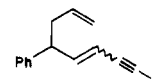
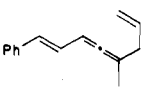
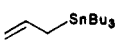
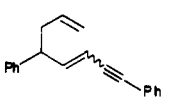
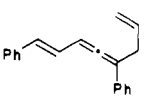
formed in the reaction. In the case of allyl palladium complex I, the η^3 structure (Ia in Scheme IIIa), which is essential[10] for external nucleophilic attack (path a), is energetically favored over its two η^1-allyl isomers (Ib, Ic), as was proved by a number of NMR studies.[10,11] In contrast, the analogous η^3-allenyl species (IIa in Scheme IIIb) is expected to be less stable than the η^1 isomers (IIb, IIc) because the palladium atom in the latter case would have to span a linear array of three carbon atoms. The preferential formation of the allenic rather than the acetylenic product reflects the greater stability of η^1-allenyl complex (IIb) relative to the η^1-propargyl isomer (IIc), as is generally known for similar derivatives of other metals.[12] The intermediacy of IIb has already been proposed by Vermeer[7c-f] for Pd-catalyzed propargylic substitution.

B. Nonconjugated Bifunctional Substrate. The above-discussed results clearly illustrate how the behavior of two chemically similar functional groups may be substantially altered by the intervention of a transition-metal catalyst. This chemoselectivity, which is attractive from the viewpoint of organic synthesis, is best taken advantage of in reactions involving bifunctional systems such as **5**. A number of representative selective alkylations of such a bifunctional compound, reacting at either the allylic or propargylic acetate function, are demonstrated in Scheme IV.

The inertness of propargylic acetate toward stabilized nucleophiles was utilized for stepwise alkylation of **5**, first with sodium dimethyl malonate to give compound **20** (still containing a propargylic acetate), followed by alkylation of the latter with phenylzinc chloride, yielding dialkylated product **21**. Since the identical Pd(0) catalyst was employed in both these reactions, it was possible to carry out the two steps in a single-pot procedure. Similarly, selective monoalkylation with tetraallylstannane gave compound **22**, which could be further alkylated with PhZnCl to yield **23**. Again, both alkylations were also performed in a single

(10) Akermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679.
(11) Godleski, S. A.; Gundlach, K. B.; Ho, H. Y.; Keinan, E.; Frolow, F. *Ibid.* **1984**, *3*, 21 and references cited therein.
(12) (a) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925. (b) Guillerm, G.; Meganem, F.; Lequan, M.; Brower, K. R. *J. Organomet. Chem.* **1974**, *67*, 43. (c) Guillerm, G.; Jean, A.; Lequan, M. *Ibid.* **1970**, *21*, P1. (d) Cochran, J. C.; Kuivila, H. G. *Organometallics* **1982**, *1*, 97. (e) Daniels, R. G.; Paquette, L. A. *Tetrahedron Lett.* **1981**, *22*, 1579. (f) Klemarczyk, P.; Rosenblum, M. *J. Org. Chem.* **1978**, *43*, 3488.

Table II. Palladium(0)-Catalyzed Substitution of Conjugated Bifunctional Substrates 6[a]

group	substrate	nucleophile	time (h)	products	yield (%)
A	**6a** (R = Me)	$NaCH(CO_2CH_3)_2$	10	 **28a** 97 **28b** 3	70
	6b (R = Ph)	$NaCH(CO_2CH_3)_2$	1	**29a** 70 **29b** 30 (*E*:*Z* = 1:3)	90
	6a		1	 **30a** 71 **30b** 29	91
B	**6a**	PhZnCl	2	 **31**	94
	6b	PhZnCl	0.2	 **32**	86
	6a		1.3	 **33**	68
	6a	MeZnCl	48	 **34**	71
	6a	Et_3Al	1	 **35**	63
C	**6a**		2	 **36a,b** 20 (*E*:*Z* = 3:1)  **36c** 80	73
	6a		3	 **37a** 36 (*E*:*Z* = 1:3)  **37b** 64	75
	6b		24	 **38a** 33 (*E*:*Z* = 1:3)  **38b** 67	57

[a] All reactions were carried out according to the general procedure given in the Experimental Section. Yields are of isolated products. Isomeric ratios were determined by ^1H NMR (270 MHz). [b] This experiment was carried out by Zeev Roth of these laboratories. The full data will be published elsewhere.

pot by sequential addition of the two nucleophiles, giving **23** in 91% yield.

Regarding the use of nonstabilized nucleophiles (vide supra) the similar reactivities of allylic and propargylic acetates pose a special challenge to the monoalkylation of compounds such as **5**. (Obviously, using excess of PhZnCl yielded a dialkylated product, **24**.) Fortunately, even the rather small difference in reactivity that favors substitution at the allylic acetate of **5** by nonstabilized nucleophiles can be amplified by carrying out the reaction at 0 °C. Thus, by using only 1 equiv of either phenylzinc chloride or vinylzinc chloride under these conditions, selective monoalkylation of the allylic functionality was achieved, yielding products **25** and **26**, respectively, in which the propargylic acetate group was untouched. These two products should undergo further alkylation. For example, treatment of **25** with Pd(0) and either PhZnCl or vinylzinc chloride led to dialkylated compounds **24** or **27**, respectively.

C. Conjugated Bifunctional Substrates. The nucleophilic attack on bifunctional substrates such as **6**, in which both the allylic and propargylic systems are conjugated by sharing the same leaving group, poses a rather complex regioselectivity problem, especially in noncatalyzed substitutions. However, the palladium-catalyzed reactions display a fairly well defined and interesting regioselectivity. Three modes of reactivity are observed, corresponding to the above-mentioned three groups of nucleophiles, each reacting with characteristic regiochemistry (A, B, and C in Table II).

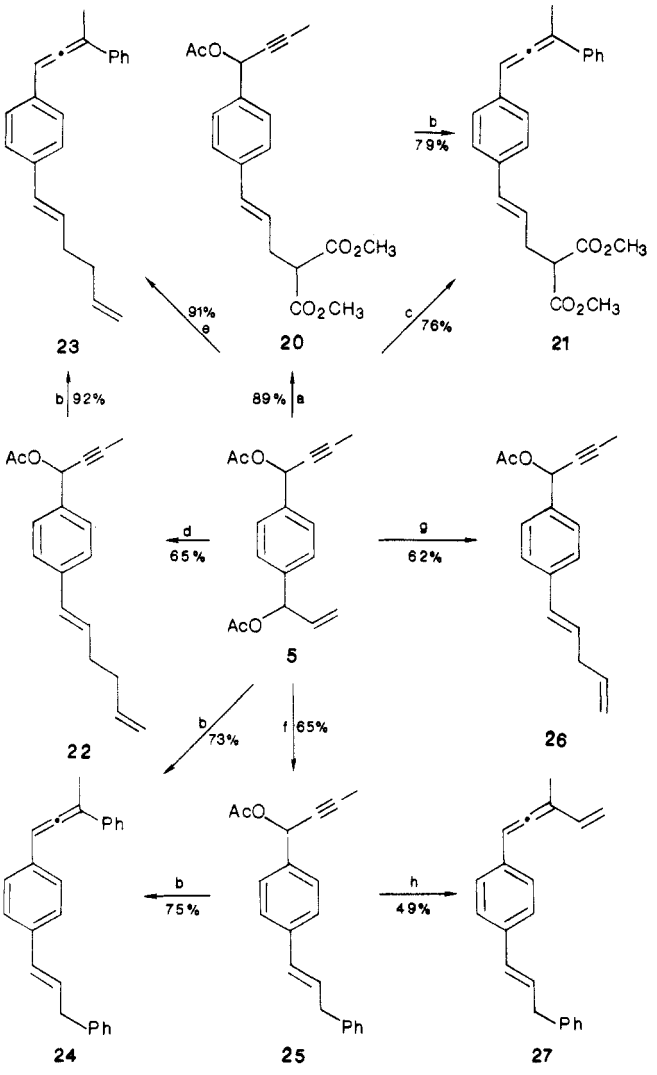
The best understood regioselectivity is that of the stabilized nucleophiles because they do not react with isolated propargylic acetates such as **1**, **3**, or **5**. Indeed, the existence of a propargylic system in **6** and **7** is ignored by these nucleophiles. They substitute the allylic system exclusively with preferential attack at the position remote from the phenyl group. This high regioselectivity is probably a result both of steric effects (attack at the less hindered position) and of formation of the thermodynamically more stable styrene isomer. It seems that the difference in electron-withdrawing properties of the phenyl and acetylene substituents is too small to effect regioselectivity.[9a]

Table III. Allylic and Propargylic Substitutions with Organocopper Reagents[a]

entry	substrate	organocopper	time (h)	R	R′	products (39:40:41)	yield (%)
1	**6a**	Me_2CuLi	12	Me	Me	10:10:80	73
2	**6b**	Me_2CuLi	2	Ph	Me	0:0:100	75
3	**6a**	Me(CN)CuLi	0.5	Me	Me	27:0:73	86
4	**6b**	Me(CN)CuLi	4	Ph	Me	54:0:46	96
5	**6a**	Bu(CN)CuLi	0.5	Me	nBu	44:4:52	76

[a] Details are given in the Experimental Section. Isomeric ratio was determined by both GC–MS and ^1H NMR (270 MHz).

Scheme IV. Palladium(0)-Catalyzed Substitution of Nonconjugated Bifunctional Substrate 5[a]



[a] All reactions were carried out according to the general procedure given in the Experimental Section (usually at room temperature unless otherwise indicated). Yields are of isolated products. (a) $NaH/CH_2(CO_2CH_3)_2$ (1.5 equiv), 1 h; (b) PhZnCl (2 equiv), $^1/_2$ h; (c) $NaH/CH_2(CO_2CH_3)_2$ (1.5 equiv), 1 h, then PhZnCl (3 equiv), 1 h; (d) tetraallylstannane (1.5 equiv), reflux 3 h; (e) tetraallylstannane (1.3 equiv), reflux 1.5 h, cooled to room temperature, PhZnCl (2 equiv), 1 h; (f) PhZnCl (1 equiv), 0 °C, 1 h; (g) vinylzinc chloride (1 equiv), 0 °C, 2 h; (h) vinylzinc chloride (1.5 equiv), 1 h.

Additionally, intramolecular coordination of the triple bond to palladium (for example, see structure IIIa in Scheme V) may account for nonsymmetrical bonding of the metal with respect to the two allylic termini. Positioning of palladium closer to the terminus bearing the phenyl group could well explain the observed attack at the opposite allylic end.

All other nuclephiles, however, can potentially react with both the allylic and propargylic electrophiles. Nevertheless, the group of nonstabilized organometallics prefer to react with the propargylic acetate moiety rather than with the allylic functionality. In agreement with the previously reported[7] and above-described results they substitute via an S_N2' mode to produce the allenic rather than the acetylenic product.

The most interesting behavior, however, is manifested by the unsaturated organotin nucleophiles such as allyl- and allenylstannanes. These compounds exhibit unique behavior[9a] which is different from that of the stabilized and nonstabilized nucleophiles. With respect to the conjugated substrate **6**, they attack via an S_N2'-type mechanism at both the allylic and propargylic moieties.[13] This behavior is even more intriguing in light of the fact that these organotin nucleophiles do not react with the simple propargylic acetates **1**, **3**, or **5**, a characteristic of the stabilized nucleophiles. Certainly, the mechanism here is more complex than mere competition between the allylic and propargylic functionalites.

In the search for a possible explanation of this unexpected behavior, it is useful to put this reaction into a more general perspective and examine similar cross-coupling processes that occur with other transition-metal compounds such as organocopper or organosilver reagents. Allylic[14] and propargylic[15] substitution by various types of organocopper reagents, for example, have been extensively studied. It is widely accepted that these reactions involve oxidative addition of the allylic or propargylic heterosubstituent to Cu(I), resulting in a Cu(III) intermediate that subsequently undergoes reductive elimination

(13) In our previous report (ref 3b) compounds **22a** and **25** were erroneously assigned an acetylenic structure. Their correct structures are the corresponding allenes **36c** and **37b** in this paper. Accordingly, the structure of compounds **23a** and **24a** in ref 3b should be corrected as well.

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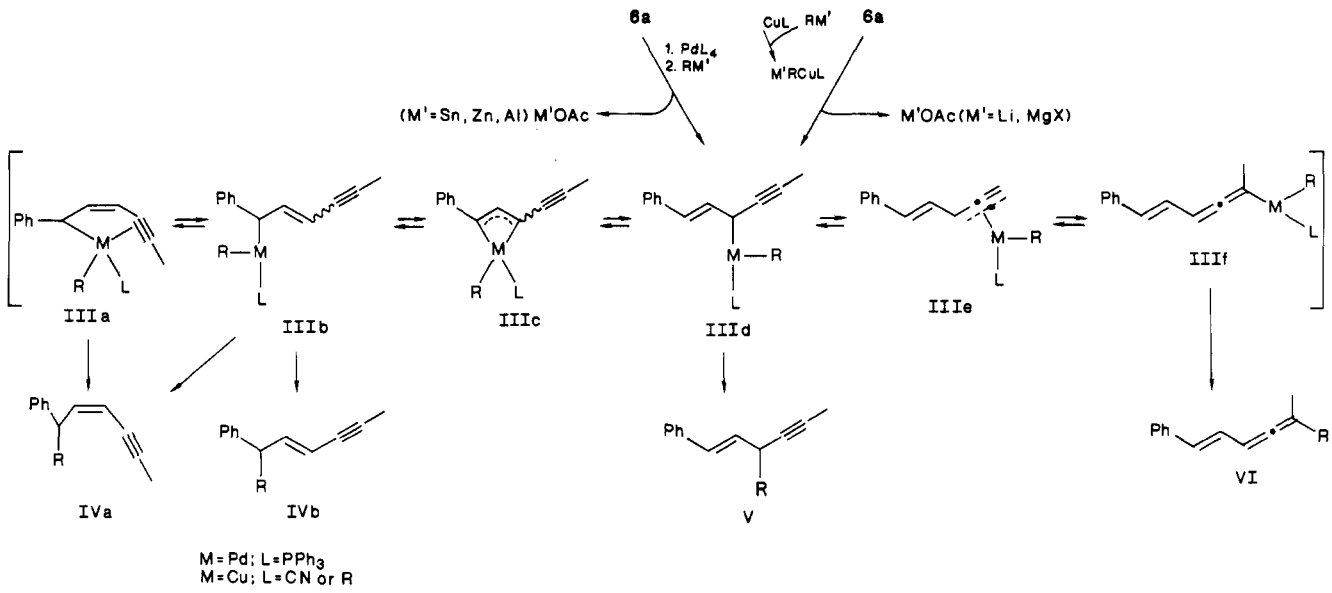
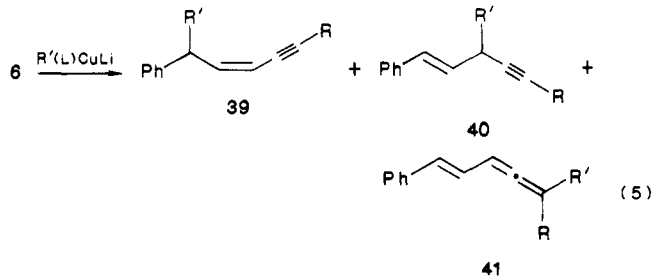
Scheme V



back to the Cu(I), forming a new C–C bond.

Interestingly, certain phenomena in organocopper chemistry are reminiscent of our observations on palladium-catalyzed substitutions, namely, the dependence of regioselectivity on the nuclephile utilized. In fact, with regard to allylic substitution by organocopper reagents, two modes of reactivity have been observed. Goering[16] reported, for example, that while allylic substitution by both homo- and heteroalkylcuprates (R_2CuLi or R(CN)CuLi) proceeds with identical stereospecificity, they react with different regioselectivities. Reaction with the former appears to proceed via a π-allyl copper intermediate, while substitution with the latter is a formal S_N2' process. Similar differences in regioselectivity (i.e., a stronger tendency to give the S_N2' product when going from R_2CuLi to R(CN)CuLi) were also observed with respect to propargylic substitution by Corey[17] and by Vermeer.[18]

We noticed that these characteristics of organocopper reagents seem to parallel our findings on palladium-catalyzed substitution of **6** with regard to two of the abovementioned groups of nucleophiles: the nonstabilized organometallics and the allyl- and allenylstannanes (see groups B and C in Table II). Therefore, in order to verify experimentally this seemingly analogous behavior, we reacted our substrate **6** with both homo- and heterocuprate reagents (eq 5 and Table III).



As may be concluded from Tables II and III, the regioselectivity associated with dimethyl cuprate (entries 1 and 2 in Table III) resembles that displayed by the group of nonstabilized organometallics (group B, Table II): both react preferentially with the propargylic function to give allenic products. Likewise, a certain similarity exists between the reactivities of the heterocuprates (entries 3–5, Table III) and that of the organotin nucleophiles (group C, Table II), namely, the tendency to react via S_N2' at both the allylic and propargylic functions. More importantly, allylic substitution with the organocopper reagents led to exclusive formation of a cis olefin (IVa in Scheme V), in agreement with earlier observations with a similar substrate.[19] This is probably the result of the relatively stable chelate intermediate IIIa. Although our palladium-catalyzed alkylations with organostannanes (group C, Table II) displayed lower stereoselectivity with respect to that newly formed double bond, an interesting preferential formation of the cis olefin was also observed, supporting the intermediacy of IIIa in the palladium case as well.

A general mechanism may be considered for the cross-coupling reaction between **6** and a nucleophilic organometallic reagent with the assistance of a transition-metal d^{10} complex such as Pd(0), Cu(I), etc. (Scheme V). Nucleophilic attack of the electron rich d^{10} complex on **6** occurs via oxidative addition of the latter to the metal (perhaps by an initial coordination of the metal to both the double and triple bonds), forming a d^8 complex. With palladium, this electrophilic d^8 adduct may react with a nonstabilized organometallic reagent RM' to form a new d^8 dialkyl complex that can exist in a number of η^1 and η^3 isomeric structures, IIIa–f. For copper, formation of the d^8 dialkyl complex III occurs by the same two steps with reversed order, namely, initial transfer of R from RM' to the metal (during generation of the organocopper reagent), followed by oxidative addition of **6** to that preformed reagent. Reductive elimination of two alkyl groups from III would result in the observed products IV–VI and the regenerated d^{10} complex.

The differences in regioselectivity of alkylation with copper and palladium probably reflect the relative rates of two types of processes: isomerization of complexes IIIa–f and reductive elimination from each, to give the products IV–VI. As was suggested by Goering,[16] the relative rates of these processes are highly dependent on the nature of

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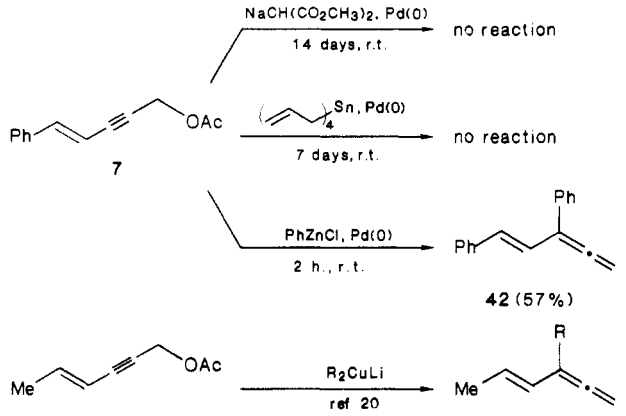
(17) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett*, **1984**, *25*, 3059, 3063.
(18) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390. Compare this work to an earlier report: Brinkmeyer, R. S.; McDonald, T. L. *J. Chem. Soc., Chem. Commun.* **1978**, 876.
(19) Descoins, C.; Henrick, C. A.; Siddall, J. B. *Tetrahedron Lett.* **1972**, 3777.

Scheme VI



the M–L moiety and on the properties of the R group. The origin of the different behavior of dialkyl cuprate and cyanoalkyl cuprate, and the similar differences between phenylzinc chloride and allylstannane, is as yet unknown. These characteristics may be correlated, perhaps, to the increasing degree of "softness" in both series.[20]

The difference in reactivity of tetraallylstannane toward nonconjugated propargylic acetates (**1**, **3**, and **5**) and the conjugated one (**6**) is remarkable. Assuming that this nucleophile reacts via path b in Scheme I, we may conclude that it is transferred efficiently to only one or two isomers of **III**, perhaps the π-allyl complex (IIIb) and probably also IIIa. This may be supported by the results shown in Scheme VI which summarizes the reaction of the three different types of nucleophiles toward compound **7**.

The same functionalities, namely, conjugated allylic and propargylic acetates, are present in both **6** and **7**, but the acetate is differently disposed. The reactivity of PhZnCl toward **7** resembles that of dialkyl cuprate,[21] both giving the allenic product. The total inertness of this substrate toward sodium dimethyl malonate and tetraallylstannane may stem from its failure to form a stable π-allyl complex which would contain an sp-hybridized carbon. Although formation of such an intermediate has been postulated by Gore,[22] it is probably less stable than the η^1-allenyl complex.

Conclusion

Palladium(0)-catalyzed substitution of propargylic acetates by various carbon nucleophiles is indeed a useful synthetic method for chemo- and regioselective formation of new C–C bonds. It is, however, less general than the analogous substitution of allylic acetates. Three modes of reactivity are observed, corresponding to three groups of nucleophiles: (a) stabilized carbanions such as sodium dimethyl malonate, which do not react with propargylic acetates but react readily with allylic acetates, (b) nonstabilized organometallics such as phenylzinc chloride which react with propargylic and allylic acetates at comparable rates (reaction with the former yielding the allenic product exclusively), and (c) allyl- and allenylstannanes (known to react with allylic acetates), which do not react with isolated propargylic acetates except for certain cases where the propargylic system is conjugated to an adjacent olefin. These observations illustrate how the behavior of two chemically similar functional groups may be substantially altered by the intervention of a transition-metal catalyst.

Experimental Section

General Methods. Elemental analyses were carried out by the microanalytical laboratory of the Hebrew University, Jerusalem. Infrared spectra were measured with an FT infrared Nicolet MX-1 spectrometer and are given in cm^{-1} units. Patterns are designated by br, broad; sh, shoulder; s, strong; w, weak; m, medium. ^1H NMR spectra were measured in deuteriochloroform (unless otherwise stated) on a Varian FT-80A or Bruker WH-270 NMR spectrometer. All chemical shifts are reported in δ units downfield from Me_4Si, and the J values are given in hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. GC–MS analyses were carried out on a Finnigan 4500 spectrometer. High resolution mass spectra were determined on a Varian Mat-731 spectrometer. Data are given in mass units with the relative intensities in parentheses. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F-254, art. 5549). Column chromatography separations were performed on silica gel (Merck, Kieselgel 60, 230-400 mesh, art. 9385) under pressure of 0.4 atm (flash chromatography). Preparative TLC was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F-254, art. 5717). GC analyses were performed on a Spectra Physics 7100 (FI detector) gas chromatograph equipped with a 0.125 in. × 2 ft column packed with 10% SE-30 on Chromosorb W. Distillations were usually performed with a Buchi Kugelrohr apparatus and the temperatures given are pot temperatures. Tetrahydrofuran and diethyl ether were distilled over sodium benzophenone ketyl. Tetrakis(triphenylphosphine)palladium was prepared from palladium dichloride.[23]

Preparation of Substrates. 1-Acetoxy-1-phenylbut-2-yne (1).[24] Allene (0.84 g, 20 mmol) was condensed into 20 mL of cold (−78 °C) THF. *n*-Butyllithium (8 mL of 1.5 M hexane solution) was added at −78 °C, and the mixture was then warmed and kept at room temperature for 4 h in order to allow complete isomerization of allenyllithium to 1-lithioprop-1-yne. The resulting cloudy white solution was cooled to 0 °C and benzaldehyde (10 mmol) was added. The mixture was stirred for $^1/_2$ h and then quenched with a saturated aqueous solution of ammonium chloride and extracted with ether. The extract was dried over magnesium sulfate and the solvent was removed under reduced pressure. Acetylation of the resulting crude alcohol with a mixture of acetic anhydride and pyridine (1:3) followed by purification by flash chromatography with hexane/ethyl acetate (6:1) yielded **1** as a colorless oil (1.5 g, 79%): NMR (80 MHz) 7.37 (m, 5 H), 6.42 (q, J = 2.1 Hz, 1 H), 2.08 (s, 3 H), 1.89 (d, J = 2.1 Hz, 3 H); IR (chloroform) 3080 (sh), 3060, 3055 (sh), 3025, 2915, 2845, 2300 (w), 2240, 1720–1750 (br), 1490, 1450, 1370, 1225 (br), 1150, 1145 (br); MS, m/e (relative intensity) 188 (13, M^+), 146 (29), 145 (21), 131 (15), 129 (30), 128 (100), 127 (24), 117 (12), 115 (10), 102 (13), 77 (19), 67 (10), 63 (10), 51 (30).

1-Acetoxy-1-phenylbut-2-ene (2).[25] Phenylmagnesium bromide (60 mmol in ether) was transferred via a canula into a cold (5 °C) solution of crotonaldehyde (4.9 mL, 60 mmol) in 50 mL of ether. The usual workup, which was followed by acetylation and flash chromatography (hexane/ethyl acetate, 10:1), afforded **2** in the form of a colorless oil (5.3 g, 46%): NMR (270 MHz) 7.35 (m, 5 H), 6.23 (d, J = 6.0 H, 1 H), 5.74 (m, 2 H), 2.09 (s, 3 H), 1.72 (d, J = 6.4 Hz, 3 H).

4-Acetoxy-6-phenylhex-2-yne (3). Allene was reacted according to the above-described procedure with *n*-butyllithium and dihydrocinnamaldehyde, followed by acetylation and purification by flash chromatography with hexane/ethyl acetate (10:1), giving **3** as a colorless oil (75%); NMR (80 MHz) 7.22 (m, 5 H), 5.27 (m, 1 H), 2.77 (m, 2 H), 2.10 (m, 2 H), 2.06 (s, 3 H); 1.86 (d, J = 2.2 Hz, 3 H); IR (neat) 3070 (sh), 3045, 3010, 2940 (sh), 2910, 2840, 2240, 2235 (sh), 1740–1760 (br s), 1595, 1490, 1425 (sh), 1360,

(20) Ho, T. L. *Tetrahedron* **1985**, *41*, 3 and references cited there.
(21) Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *J. Organomet. Chem.* **1980**, *192*, 275.
(22) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 203.
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(24) Kawai, K. I.; Imuta, M.; Ziffer, H. *Tetrahedron Lett.* **1981**, *22*, 2527.
(25) Goering, H. L.; Seitz, E. P., Jr.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304.

1220–1240 (br s), 1030; MS, *m/e* (relative intensity) 174 (15), 158 (20), 156 (39), 155 (26), 141 (100), 129 (22), 118 (29), 117 (24), 91 (68); HRMS, calcd for $C_{12}H_{12}$ (M^+ – AcOH) 156.0939, found 156.0946.

4-Acetoxy-6-phenylhex-2-ene (4a). Phenethylmagnesium bromide (prepared from phenethyl bromide and magnesium) in 100 mL of ether was added to crotonaldehyde as described above. Acetylation followed by chromatography (hexane/ethyl acetate, 20:1) afforded **4a** as a colorless oil (58%): NMR (270 MHz) 7.21 (m, 5 H), 5.74 (dq, J = 15.2, 6.5 Hz, 1 H), 5.43 (ddq, J = 15.2, 7.3, 1.5 Hz, 1 H), 5.21 (q, J = 6.8 Hz, 1 H), 2.62 (t, J = 7.7 Hz, 2 H), 2.02 (s, 3 H), 1.97 (m, 2 H), 1.70 (dd, J = 6.5, 1.5 Hz, 3 H); IR (neat) 3070 (sh), 3030 (sh), 3005, 2990 (sh), 2920 (br), 2840, 1730–1715 (br), 1665, 1590, 1485, 1445 (br), 1365, 1220–1250 (br); MS, *m/e* (relative intensity) 159 (22), 158 (89), 144 (16), 143 (79), 129 (96), 128 (16), 105 (25), 92 (16), 91 (90), 71 (59), 65 (22), 43 (100); HR MS, calcd for $C_{12}H_{14}$ (M^+ – AcOH) 158.1095, found 158.1110.

3-Acetoxy-5-phenylpent-1-ene (4b). Vinylmagnesium bromide (33 mmol) was added to a solution of 30 mmol of dihydrocinnamaldehyde in THF. The reaction was worked up and acetylated as usual followed by M^+ chromatography with hexane/ethyl acetate (10:1) to give **4b** as a colorless oil: NMR (80 MHz) 7.2 (m, 5 H), 5.85 (ddd, J = 17, 10, 6 Hz, 1 H), 5.29 (m, 1 H), 5.28 (br d, J = 10 Hz, 1 H), 5.23 (br d, J = 17 Hz, 1 H), 2.67 (br t, J = 7.5 Hz, 2 H), 2.05 (s, 3 H), 1.96 (br t, J = 7.5 Hz, 2 H); IR (neat) 3090, 3065, 3030, 2990, 2935, 1740, 1650, 1605, 1500, 1455, 1370, 1240, 1025, 990, 930, 790, 700; MS, *m/e* (relative intensity) 144 (49, M^+ – AcOH), 143 (21), 130 (10), 129 (100), 128 (11), 105 (17), 92 (11), 91 (85), 77 (17), 66 (55), 65 (34), 57 (12), 51 (20).

1-(1-Acetoxyprop-2-enyl)-4-(1-acetoxybut-2-ynyl)benzene (5). Allene (2.0 g, 50 mmol) was condensed into 50 mL of THF at –78 °C followed by addition of *n*-butyllithium (30 mL, 45 mmol). After warming to room temperature, the solution was transferred via a canula into a solution of terephthalaldehyde (6.03 g, 45 mmol) in 50 mL of THF. The mixture was worked up as described above and the product (monoaldehyde) was purified by flash chromatography and then dissolved in 60 mL of THF. A solution of vinylmagnesium bromide (75 mmol) in 50 mL of THF was added and the mixture was stirred for $^1/_2$ h followed by the usual workup. The crude diol was purified by flash chromatography and then acetylated and purified by chromatography to give **5** as a colorless oil (3.15 g, 28%): NMR (270 MHz) 7.41 (m, 4 H), 6.45 (q, J = 2.2 Hz, 1 H), 6.29 (d, J = 6.4 Hz, 1 H), 6.02 (m, 1 H), 5.34 (d, J = 16.8 Hz, 1 H), 5.24 (d, J = 18.0 Hz, 1 H), 2.12 (s, 6 H), 1.93 (d, J = 2.2 Hz, 3 H); IR (neat) 3020, 2924, 2857, 2239, 1739 (s), 1645, 1514, 1425, 1371, 1227 (s), 1019, 983, 955, 844, 826, 803; MS, *m/e* (relative intensity) 286 (6, M^+), 227 (15), 226 (40), 185 (23), 184 (100), 183 (23), 167 (26), 166 (28), 165 (52), 155 (36), 152 (22), 141 (28), 128 (23), 115 (43), 82 (17), 77 (17), 67 (35), 55 (52), 51 (21); HRMS, calcd 286.1205, found 286.1260.

4-Acetoxy-6-phenylhex-5-en-2-yne (6a). The compound was prepared as described in ref 3b from allene and cinnamaldehyde in pure THF without HMPA. Acetylation followed by Kugelrohr distillation (170 °C/0.3 mm) gave **6a** in 56% yield.

3-Acetoxy-1,5-diphenylpent-4-en-1-yne (6b). Phenylacetylene (3 mL, 27 mmol) was dissolved in 15 mL of ether and cooled to –15 °C. *n*-Butyllithium (16 mL of 1.5 M solution in hexane) was added followed by cinnamaldehyde (3 mL, 22.5 mmol). Acetylation with subsequent flash chromatography afforded **6b** in the form of colorless oil (3.6 g, 57 %): NMR (270 MHz) 7.5–7.3 (m, 10 H), 6.92 (dm, J = 15.3 Hz, 1 H), 6.32 (dd, J = 15.3, 6.6 Hz, 1 H), 6.30 (br d, J = 6.6 Hz, 1 H), 2.15 (s, 3 H); IR (neat) 3080 (sh), 3050 3020, 2930 (w), 2250, 2225, 1725–1750 (s, br), 1645 (w), 1595, 1575 (w), 1490, 1445, 1440, 1370, 1210–1240 (s, br), 1010, 965.

1-Acetoxy-5-phenylpent-4-en-2-yne (7).[26] Bromostyrene (2.56 mL, 20 mmol) was added to 50 mL of diethylamine under inert conditions. Thereafter 93 mg (0.08 mmol) of $Pd(PPh_3)_4$ and 49 mg (0.26 mmol) of copper(I) iodide were $Pd(PPh_3)_4$ Finally 1.2 mL (20 mmol) of propargyl alcohol was added over a period of 20 min. The mixture was stirred for 24 h after which the diethylamine was removed under reduced pressure. The residue was dissolved in benzene and passed through a neutral alumina column. The crude alcohol (NMR given below) was acetylated and purified by flash chromatography with hexane/ethyl acetate (4:1), yielding 1.74 g (44%) of **7** as an orange oil.

NMR of 5-phenylpent-4-en-2-yn-1-ol (80 MHz): 7.33 (m, 5 H), 6.96 (d, J = 16.2 Hz, 1 H), 6.16 (dt, J = 16.2, 2.0 Hz, 1 H), 4.44 (d, J = 2.0 Hz, 2 H), 1.6 (br s, 1 H).

NMR of 7 (80 MHz): 7.33 (m, 5 H), 7.00 (d, J = 16.2 Hz, 1 H), 6.14 (dt, J = 16.2, 2.0 Hz, 1 H), 4.85 (d, J = 2.0 Hz, 2 H), 2.11 (s, 3 H). IR (neat): 3040 (sh), 3010, 2920, 2200, 1730-1745 (br), 1485, 1400, 1425 (sh), 1375, 1355, 1265, 1220–1240 (br), 1160.

Preparation of Nucleophiles. Tetraallylstannane,[27] allyltributylstannane,[28] and allenyltributylstannane[3b] were prepared as reported. The organozinc reagents were prepared by mixing the corresponding lithium or magnesium reagents with anhydrous zinc chloride in either THF or ether solution. For example, phenylzinc chloride was prepared by adding phenylmagnesium bromide (4 mmol) to a solution of anhydrous zinc chloride (4 mmol) in THF (7 mL). The exothermic reaction was accompanied by copious precipitation of magnesium halide. The liquid layer was taken and used as a solution of 4 mmol phenylzinc chloride. In a similar manner, vinylzinc chloride was prepared from vinylmagnesium bromide. Methylzinc chloride and 1-propynylzinc chloride were prepared from the corresponding lithium compounds. Diethylaluminium chloride (2 M solution in hexane–benzene) was purchased from Aldrich. Diethyl(1-heptynyl)aluminum was prepared by addition of *n*-butyllithium to a THF solution of 1-heptyne followed by adding the resulting mixture to a THF solution of diethylaluminum chloride.

General Procedure for Palladium-Catalyzed Reactions. All reactions were carried out in flame-dried glassware under argon atmosphere. A THF solution (3 mL) of the nucleophile (1.5–2 mmol) was added to a solution of the substrate (1 mmol) and $Pd(PPh_3)_4$ (5–7 mol %) in 3 mL of THF. When the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure and the residue was subjected to flash chromatography (using an appropriate mixture of hexane and ethyl acetate). More details are given in the equations and tables. Spectroscopic data of the products are given below.

1,3-Diphenylbuta-1,2-diene (8): NMR (270 MHz) 7.3 (m, 10 H), 6.46 (q, J = 2.9 Hz, 1 H), 2.22 (d, J = 2.9 Hz, 3 H); IR (neat) 3060, 3040, 3010, 2970, 2930, 2905, 2840 (sh), 1930, 1590, 1485, 1460 (sh), 1360, 1060, 1025; MS *m/e* (relative intensity) 206 (90, M^+), 205 (20), 192 (16), 191 (100), 190 (15), 189 (25), 165 (18), 128 (26), 95 (19), 91 (29), 89 (22), 82 (16), 77 (27), 63 (17), 51 (39). Anal. Calcd: C 93.20; H, 6.80. Found: C, 92.76; H, 7.23.

Methyl 2-(methoxycarbonyl)-3-methyl-5-phenylpent-4-enoate (9): NMR (270 MHz) 7.3 (m, 5 H), 6.47 (d, J = 15.8 Hz, 1 H), 6.04 (dd, J = 15.8, 7.6 Hz, 1 H), 3.74 (s, 3 H), 3.66 (s, 3 H), 3.39 (d, J = 7.5 Hz, 1 H), 3.18 (br sextet, J = 7 Hz, 1 H), 1.18 (d, J = 6.5 Hz, 3 H); IR 3055 (sh), 3020, 2945 (s), 2875 (sh), 2840 (sh), 1720–1760 (s, br), 1595, 1490, 1460 (sh), 1445 (sh), 1430 (s), 1130–1330 (s, br), 1070, 1030 (sh), 1020, 970; MS, *m/e* (relative intensity) 262 (4, M^+), 143 (86), 142 (24), 131 (100), 129 (29), 128 (35), 116 (14), 115 (28), 91 (77), 77 (24), 69 (13), 65 (19), 59 (31), 53 (18), 51 (28).

1,3-Diphenylbut-1-ene (10):[29] NMR (270 MHz) 7.3 (m, 10 H), 6.39 (br s, 2 H), 3.67 (m, 1 H), 1.46 (d, J = 7.0 Hz, 3 H); IR (neat) 3075, 3050, 3020, 2990 (sh), 2960, 2920, 2860, 1940 (br), 1865 (br), 1800 (br), 1740 (br), 1590, 1570 (sh), 1560 (sh), 1490, 1480, 1470 (sh), 1450, 1440 (sh), 1430, 1370, 1155, 1070, 1020 (sh), 1010, 965, 900; MS *m/e* (relative intensity) 208 (27, M^+), 193 (27), 178 (11), 130 (20), 129 (12), 116 (12), 115 (100), 91 (55), 89 (13), 78 (12), 77 (28), 65 (23), 63 (14), 51 (38).

2,6-Diphenylhexa-2,3-diene (11): NMR (270 MHz) 7.24 (m, 10 H), 5.46 (br tq, J = 7, 3 Hz, 1 H), 2.79 (t, J = 7.2 Hz, 2 H), 2.44 (m, 2 H), 2.01 (d, J = 2.9 Hz, 3 H) [Irradiation at 5.46 ppm generated the following changes: 2.01 (s, 3 H), 2.44 (br t, J = 7

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Hz, 2 H).]; IR (methylene chloride) 3090 (sh), 3070, 3040, 2990 (sh), 2930, 2865, 1955 (sh), 1950, 1735 (w), 1605 (sh), 1600, 1500, 1460, 1450, 1380 (w), 1270; MS, *m/e* (relative intensity) 234 (32, M^+), 219 (17), 206 (11), 143 (38), 142 (11), 141 (19), 130 (11), 129 (40), 128 (80), 127 (18), 115 (32), 105 (17), 103 (17), 92 (12), 91 (100), 77 (31), 65 (33), 63 (12), 51 (36). Anal. Calcd: C, 92.30; H, 7.69. Found: C, 92.13; H, 7.87.

Methyl 2-(Methoxycarbonyl)-3-methyl-7-phenylhept-4-enoate (12a) and Methyl 2-(Methoxycarbonyl)-5-phenyl-3-propenylpentanoate (12b). NMR of **12a** (270 MHz): 7.2 (m, 5 H), 5.56 (dt, *J* = 15.5, 6.0 Hz, 1 H), 5.38 (dd, *J* = 15.5, 8.0 Hz, 1 H), 3.71 (s, 3 H), 3.66 (s, 3 H), 3.25 (d, *J* = 7.5 Hz, 1 H), 2.90 (br sextet, *J* = 7 Hz, 1 H), 2.63 (t, *J* = 8.0 Hz, 2 H), 2.29 (br q, *J* = 8 Hz, 2 H), 1.04 (d, *J* = 6.5 Hz, 3 H). NMR of **12b** (partial spectrum): 3.69 (s, 3 H), 3.66 (s, 3 H), 3.36 (d, *J* = 8.0 Hz, 1 H), 1.68 (dd, *J* = 5.0, 1.2 Hz, 3 H). IR of **12a + 12b**: 3020, 2995 (sh), 2940, 2840, 1720–1760 (s, br), 1600, 1490, 1460 (sh), 1450, 1430, 1135–1340 (s, br), 1020, 970. MS of **12a**, *m/e* (relative intensity): 158 (12), 139 (14), 125 (13), 107 (16), 91 (100), 81 (11), 79 (43), 67 (16), 65 (26), 59 (29), 55 (18), 53 (12). MS of **12b**, *m/e* (relative intensity): 129 (21), 105 (20), 104 (53), 92 (11), 91 (100), 79 (20), 77 (17), 69 (11), 67 (22), 65 (27), 59 (25), 55 (24), 53 (12).

1,5-Diphenylhex-3-ene (13a) and 4,6-Diphenylhex-2-ene (13b). NMR of **13a** (270 MHz): 7.3 (m, 10 H), 5.4 (m, 2 H), 3.5 (br quintet, *J* = 6.5 Hz, 1 H), 2.6 (t, *J* = 7 Hz, 2 H), 2.3 (br q, *J* = 7 Hz, 2 H), 1.3 (d, *J* = 7.0 Hz, 3 H). NMR of **13b**: 7.3 (m, 10 H), 5.4 (m, 2 H), 3.1 (br q, *J* = 7 Hz, 1 H), 2.5 (t, *J* = 7 Hz, 2 H), 1.9 (q, *J* = 7.0 Hz, 2 H), 1.66 (d, *J* = 4.7 Hz, 3 H). IR of **13a + 13b** (chloroform): 3070 (sh), 3050, 3020, 2960, 2920, 2850, 1600, 1480, 1450, 1430, 1025, 965, 905. MS of **13a**, *m/e* (relative intensity): 236 (2, M^+), 145 (26), 131 (22), 129 (10), 118 (37), 117 (32), 115 (13), 106 (11), 105 (30), 92 (12), 91 (100), 77 (18), 65 (31), 51 (17). MS of **13b**, *m/e* (relative intensity) 236 (4, M^+), 132 (13), 131 (100), 115 (14), 105 (16), 92 (14), 91 (80), 77 (20), 65 (24), 53 (12), 51 (18).

1-Phenyl-3-methylpenta-1,2,4-triene (14):[30] NMR (270 MHz) 7.3 (m, 5 H), 6.39 (dd, *J* = 17, 11 Hz, 1 H), 6.24 (m,, 1 H), 5.22 (br d, *J* = 17 Hz, 1 H), 5.10 (br d, *J* = 11 Hz, 1 H), 1.93 (d, *J* = 2.9 Hz, 3 H); MS, *m/e* (relative intensity) 156 (100, M^+), 155 (44), 153 (18), 141 (88), 129 (25), 128 (40), 127 (16), 115 (89), 91 (37), 78 (30), 77 (41), 76 (20), 63 (31), 51 (58).

3-Methyl-7-phenylhepta-1,3,4-triene (15): NMR (270 MHz) 7.3 (m, 5 H), 6.24 (ddd, *J* = 17.4, 10.6, 1.0 Hz, 1 H), 5.23 (m, 1 H), 5.03 (br d, *J* = 17.4 Hz, 1 H), 4.98 (br d, *J* = 10.6 Hz, 1 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 2.33 (br q, *J* = 7.5 Hz, 2 H), 1.73 (d, *J* = 2.7 Hz, 3 H) [Irradiation at 5.23 ppm caused the following changes: 6.24 (dd, *J* = 17.4, 10.6 Hz, 1 H), 2.33 (t, *J* = 7.6 Hz, 2 H), 5.03 (d, *J* = 17.4 Hz, 1 H), 4.98 (d, *J* = 10.6 Hz, 1 H), 1.73 (s, 3 H).]; IR (neat) 3100, 3080, 3060, 3040, 2940 (br), 2870, 2300 (w), 1940 (s), 1800 (br), 1610, 1495, 1455, 1450 (sh), 1370 (w), 1335 (w), 1270 (s), 1240, 1200 (w); MS, *m/e* (relative intensity) 184 (6, M^+), 169 (43), 156 (26), 155 (16), 154 (12), 141 (28), 129 (17), 128 (14), 115 (10), 93 (17), 92 (11), 91 (100), 79 (15), 78 (20), 77 (81), 65 (43), 63 (10).

The product was hydrogenated under hydrogen gas (1 atm) using catalytic amounts of 10% Pd/C in ethyl acetate at room temperature, followed by purification by flash chromatography with hexane.

1-Phenyl-5-methylheptane was obtained as a sole product: NMR (80 MHz) 7.20 (m, 5 H), 2.60 (t, *J* = 7.4 Hz, 2 H), 1.6–0.7 (m, 15 H); MS, *m/e* (relative intensity) 190 (13, M^+), 133 (7), 105 (9), 93 (8), 92 (100), 91 (98), 79 (5), 78 (6), 77 (6), 65 (13), 57 (50), 55 (10), 51 (6).

1-Phenyl-5-methyloct-6-yne-3,4-diene (16): NMR (80 MHz) 7.2 (m, 5 H), 5.27 (m, 1 H), 2.74 (t, *J* = 7.5 Hz, 2 H), 2.37 (br q, *J* = 7.5 Hz, 2 H), 1.93 (d, *J* = 1.2 Hz, 3 H), 1.73 (d, *J* = 3.0 Hz, 3 H); IR (methylene chloride) 3095 (sh), 3085 (sh), 3025, 2950 (sh), 2930, 2860, 2410 (w), 2245 (w), 1950 (w), 1715–1760 (br), 1605, 1500, 1455, 1380, 1225; MS, *m/e* (relative intensity) 196 (2, M^+), 182 (15), 181 (97), 180 (10), 179 (13), 167 (49), 166 (63), 165 (77), 153 (24), 152 (13), 141 (13), 129 (11), 128 (15), 115 (16), 103 (22), 91 (79), 89 (14), 79 (29), 78 (20), 77 (81), 65 (100), 64 (11), 63 (37), 53 (31), 52 (16), 51 (72).

2-Methyl-6-phenylhexa-2,3-diene (17): NMR (270 MHz) 7.2 (m, 5 H), 4.98 (m, 1 H), 2.70 (t, *J* = 7.5 Hz, 2 H), 2.26 (br q, *J* = 7.5 Hz, 2 H), 1.62 (d, *J* = 2.8 Hz, 6 H); IR (neat) 3085 (sh), 3060 (sh), 3030 (sh), 2980 (sh), 2920 (br), 2860, 1965 (br), 1935 (sh), 1730 (w), 1600, 1585 (sh), 1495, 1450, 1410 (w), 1365, 1190. MS, *m/e* (relative intensity) 172 (2, M^+), 157 (19), 143 (7), 142 (12), 130 (14), 129 (100), 128 (20), 115 (11), 104 (7), 91 (63), 81 (18), 79 (49), 78 (7), 77 (21), 65 (38), 63 (9), 55 (11), 53 (51), 52 (7), 51 (25).

5-Methyl-1-phenyldodeca-3,4-diene-6-yne (18): NMR (270 MHz) 7.3 (m, 5 H), 5.32 (m, 1 H), 2.76 (t, *J* = 7.5 Hz, 2 H), 2.31 (br q, *J* = 7.5 Hz, 2 H), 1.74 (d, *J* = 2.9 Hz, 3 H), 1.54 (m, 2 H), 1.31 (m, 6 H), 0.90 (t, *J* = 6.5 Hz, 3 H); IR (neat) 3090, 3070, 3030, 2960–2860 (br), 2230, 1945, 1740 (w), 1600, 1500, 1460, 1440, 1380, 1370, 1330, 1240 (br), 1030, 740, 700.

1-Phenyl-3-methylpenta-1,2-diene (19):[31] NMR (80 MHz) 7.3 (m, 5 H), 6.08 (m, 1 H), 2.09 (m, 2 H), 1.82 (d, *J* = 2.6 Hz, 3 H), 1.05 (t, *J* = 7.3 Hz, 3 H); IR (neat) 3080, 3060, 3020, 2960, 2920, 2840 (sh), 1940, 1930 (sh), 1590, 1490, 1450, 1370, 1360, 1320, 1260, 1070, 1020, 910, 820.

Methyl 2-(methoxycarbonyl)-5-[4-(1-acetoxybut-2-ynyl)-phenyl]pent-4-enoate (20): NMR (270 MHz) 7.40 (br d, *J* = 8 Hz, 2 H), 7.31 (br d, *J* = 8 Hz, 2 H), 6.47 (br d, *J* = 15.8 Hz, 1 H), 6.38 (q, *J* = 2.2 Hz, 1 H), 6.15 (dt, *J* = 15.8, 7.2 Hz, 1 H), 3.84 (s, 6 H), 3.53 (t, *J* = 7.5 Hz, 1 H), 2.81 (td, *J* = 7.4, 1.1 Hz, 2 H), 2.09 (s, 3 H), 1.90 (d, *J* = 2.3 Hz, 3 H).

Methyl 2-(methoxycarbonyl)-5-[4-(3-phenylbuta-1,2-dienyl)phenyl]pent-4-enoate (21): NMR (270 MHz) 7.5–7.2 (m, 9 H), 6.42 (d, *J* = 16 Hz, 1 H), 6.41 (q, *J* = 2.8 Hz, 1 H), 6.10 (dt, *J* = 16, 7 Hz, 1 H), 3.70 (s, 6 H), 3.51 (t, *J* = 7 Hz, 1 H), 2.77 (t, *J* = 7 Hz, 2 H), 2.20 (d, *J* = 2.8 Hz, 3 H); IR (neat) 3060, 3020, 3000, 2970, 2880, 2380, 1950, 1790–1710 (br), 1620, 1530, 1510, 1480, 1450, 1360, 1290, 1250, 1220, 1180, 1110, 1080, 1045, 990, 930, 880, 780, 750, 710, 660, 620.

1-Acetoxy-1-[4-(hexa-1,5-dienyl)phenyl]but-2-yne (22): NMR (80 MHz) 7.47 (d, *J* = 8 Hz, 2 H), 7.33 (d, *J* = 8 Hz, 2 H), 6.44 (d, *J* = 15.4 Hz, 1 H), 6.38 (q, *J* = 2.2 Hz, 1 H), 6.1 (dt, *J* = 15.4, 7 Hz, 1 H), 5.8 (m, 1 H), 5.03 (br d, *J* = 17 Hz, 1 H), 4.99 (br d, *J* = 11 Hz, 1 H), 2.27 (m, 4 H), 2.07 (s, 3 H), 1.89 (d, *J* = 2.2 Hz, 3 H).

3-Phenyl-1-[4-(hexa-1,5-dienyl)phenyl]buta-1,2-diene (23): NMR (270 MHz) 7.5–7.2 (m, 9 H), 6.48 (q, *J* = 2.9 Hz, 1 H), 6.40 (br d, *J* = 15.8 Hz, 1 H), 6.22 (dt, *J* = 15.8, 6.8 Hz, 1 H), 5.90 (m, 1 H), 5.06 (br d, *J* = 17 Hz, 1 H), 5.00 (br d, *J* = 11 Hz, 1 H), 2.27 (m, 4 H), 2.22 (d, *J* = 2.9 Hz, 3 H).

3-Phenyl-1-[4-(3-phenylprop-1-enyl)phenyl]buta-1,2-diene (24): NMR (270 MHz) 7.6–7.2 (m, 14 H), 6.44 (q, *J* = 2.9 Hz, 1 H), 6.41 (d, *J* = 16 Hz, 1 H), 6.32 (dt *J* = 16, 6.1 Hz, 1 H), 3.53 (d, *J* = 6.1 Hz, 2 H), 2.21 (d, *J* = 2.9 Hz, 3 H); IR (neat) 3027, 2920, 1934, 1602, 1493, 1453, 967, 851, 758, 698; HRMS, calcd for $C_{25}H_{22}$ 322.1721, found 322.1652.

1-Acetoxy-1-[4-(3-phenylprop-1-enyl)phenyl]but-2-yne (25): NMR (270 MHz) 7.5–7.2 (m, 9 H), 6.45 (d, *J* = 16 Hz, 1 H), 6.38 (q, *J* = 2.1 Hz, 1 H), 6.35 (dt, *J* = 16, 6.1 Hz, 1 H), 3.53 (d, *J* = 6.1 Hz, 2 H), 2.09 (s, 3 H), 1.90 (d, *J* = 2.1 Hz, 3 H); IR (neat) 3027, 2957, 2927, 2239, 1738 (s), 1605, 1495, 1453, 1379, 1362, 1227 (s), 1028, 1018, 968, 699; HRMS, calcd for $C_{21}H_{20}O_2$ 304.1463, found 304.1441.

1-Acetoxy-1-[4-(penta-1,4-dienyl)phenyl]but-2-yne (26): NMR (80 MHz) 7.4 (m, 4 H), 6.45 (d, *J* = 16 Hz, 1 H), 6.39 (q, *J* = 2.3 Hz, 1 H), 6.18 (dt, *J* = 16, 5.7 Hz, 1 H), 5.80 (m, 1 H), 5.07 (br d, *J* = 16.4 Hz, 1 H), 5.04 (br d, *J* = 11.2 Hz, 1 H), 2.95 (br t, *J* = 5.7 Hz, 2 H), 2.07 (s, 3 H), 1.90 (d, *J* = 2.3 Hz, 3 H).

3-Methyl-1-[4-(3-phenylprop-1-enyl)phenyl]penta-1,2,4-triene (27): NMR (270 MHz) 7.3–7.1 (m, 9 H), 6.43 (br d, *J* = 16 Hz, 1 H), 6.35 (m, 2 H), 6.23 (m, 1 H), 5.24 (d, *J* = 17 Hz, 1 H), 5.12 (d, *J* = 11 Hz, 1 H), 3.55 (d, *J* = 6.0 Hz, 2 H), 1.92 (d, *J* = 2.8 Hz, 3 H).

1-Phenyl-3-(bis(methoxycarbonyl)methyl)hex-1-en-4-yne (28a): NMR (270 MHz) 7.35–7.15 (m, 5 H), 6.63 (br d, *J* = 15.6 Hz, 1 H), 6.11 (dd, *J* = 15.6, 7.1 Hz, 1 H), 3.96 (tm, *J* = 7.5 Hz, 1 H), 3.78 (s, 3 H), 3.71 (s, 3 H), 3.58 (d, *J* = 8.4 Hz, 1 H), 1.84 (d, *J* = 2.4 Hz, 3 H); IR (neat) 3060, 3040, 3000, 2960, 2930, 2850,

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2310, 2260, 1760–1730 (br, s), 1600, 1500, 1450, 1435, 1340–1140 (br), 1030, 970, 910, 850, 740 (s), 700 (s); MS, *m/e* (relative intensity) 286 (0.6, M^+), 228 (16), 227 (100), 211 (17), 195 (13), 194 (10), 168 (10), 167 (51), 166 (17), 165 (33), 155 (94), 154 (24), 153 (50), 152 (50), 141 (10), 129 (24), 128 (37), 127 (24), 115 (63), 103 (8), 102 (13), 91 (38), 89 (11), 77 (44), 69 (33), 65 (24), 63 (21), 59 (68), 51 (43); MS (chemical ionization), *m/e* 287 ($M^+ + 1$). The isomeric product **28b** was detected in trace quantities (less than 3%) by both NMR (in analogy to **29b**) and GC–MS analysis.

1,5-Diphenyl-3-(bis(methoxycarbonyl)methyl)pent-1-en-4-yne (29a) and 1,5-diphenyl-1-(bis(methoxycarbonyl)-methyl)pent-2-en-4-yne (29b): NMR of **29a** (270 MHz) 7.3 (m, 10 H), 6.81 (d, J = 15.7 Hz, 1 H), 6.22 (dd, J = 15.6, 6.9 Hz, 1 H), 4.25 (dd, J = 8.3, 6.9 Hz, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.73 (d, J = 8.3 Hz, 1 H). NMR of **29b** (270 MHz) (partial spectrum): 6.18 (t, J = 10 Hz) and 6.37 (dd, J = 16, 8.5 Hz), at a 2.5:1 ratio, together 1 H, 5.77 (d, J = 10 Hz) and 5.76 (d, J = 16 Hz), at a 2.5:1 ratio, together 1 H, 4.83 (br t, J = 10 Hz, 1 H), 3.97 (d, J = 10 Hz, 1 H). IR of **29a + 29b** (chloroform): 3080, 3060, 3020, 3000, 2950, 2360, 1760–1725 (br s), 1590, 1485, 1450 (sh), 1440 (sh), 1430, 1340–1150 (br s), 1030, 1020 (sh), 965, 910. MS of **29a + 29b** *m/e* (relative intensity): 348 (16), 289 (77), 284 (17), 257 (29), 230 (21), 229 (54), 217 (100), 215 (71), 115 (48), 108 (15), 105 (40), 101 (11), 91 (23), 77 (16); HRMS, calcd for $C_{22}H_{20}O_4$ 348.1361, found 348.1320.

1,5-Diphenylhexa-1,3,4-triene (31): NMR (270 MHz) 7.4 (m, 10 H), 6.66 (dd, J = 15.8, 9.7 Hz, 1 H), 6.54 (d, J = 15.8 Hz, 1 H), 6.29 (dq, J = 9.7, 2.9 Hz, 1 H), 2.14 (d, J = 2.9 Hz, 3 H); IR (methylene chloride) 3080, 3050, 3020, 2980, 2920, 1940, 1935 (sh), 1590, 1495 (sh), 1490, 1480, 1445, 1440 (sh), 1430 (sh), 1370 (w), 1270 (w), 1180 (w), 1065, 1025; MS, *m/e* (relative intensity) 232 (100, M^+), 217 (75), 215 (56), 216 (30), 202 (47), 153 (19), 141 (21), 128 (32), 115 (62), 108 (37), 103 (20), 91 (61), 77 (47). Anal. Calcd: C, 93.88; H, 6.12. Found: C, 93.35; H, 6.53.

1,1,5-Triphenylpenta-1,2,4-triene (32): NMR (270 MHz) 7.5–7.2 (m, 15 H), 6.76 (dd, J = 15.5, 10.0 Hz, 1 H), 6.63 (d, J = 15.5 Hz, 1 H), 6.55 (d, J = 10.0 Hz, 1 H); IR (neat) 3070 (sh), 3050, 3020, 2320 (w), 2250 (w), 1930 (w), 1590, 1570 (w), 1490, 1485, 1480 (sh), 1470, 1450, 1440, 1430, 1075, 1065, 1030, 1000 (w), 960, 910; MS, *m/e* 294 (M^+).

5-Methyl-1-phenylhepta-1,3,4,6-tetraene (33): NMR (270 MHz) 7.3 (m, 5 H), 6.59 (dd, J = 14.9, 8.9 Hz, 1 H), 6.48 (d, J = 14.9 Hz, 1 H), 6.38 (dd, J = 17.2, 10.4 Hz, 1 H), 6.12 (dm, J = 8.9 Hz, 1 H), 5.14 (d, J = 17.2 Hz, 1 H), 5.08 (d, J = 10.4 Hz, 1 H), 1.88 (d, J = 2.5 Hz, 3 H); IR (neat) 3080 (sh), 3050 (sh), 3020, 2980, 2920, 2300 (w), 1940, 1810 (w), 1610, 1590, 1490, 1445, 1370, 1265, 1070 (w), 1030 (w), 985 (sh), 965, 900; MS, *m/e* (relative intensity) 182 (38, M^+), 181 (13), 168 (10), 167 (91), 166 (43), 165 (77), 153 (23), 152 (61), 141 (14), 128 (29), 115 (51), 102 (14), 91 (21), 89 (25), 78 (18), 77 (48), 76 (21), 75 (15), 74 (11), 65 (33), 63 (57), 62 (14), 53 (23), 52 (22), 51 (100).

5-Methyl-1-phenylhexa-1,3,4-triene (34): NMR (270 MHz) 7.3 (m, 5 H), 6.59 (dd, J = 15.7, 9.9 Hz, 1 H), 6.44 (d, J = 15.7 Hz, 1 H), 5.85 (dm, J = 9.9 Hz, 1 H), 1.76 (d, J = 2.8 Hz, 6 H); IR (neat) 3080 (sh), 3060 (sh), 3030, 2980, 2930 (sh), 2910, 2870 (sh), 2860, 1940, 1595, 1495, 1445, 1260, 1220; MS, *m/e* (relative intensity) 170 (47, M^+), 156 (13), 155 (100), 154 (21), 153 (26), 152 (12), 141 (17), 129 (27), 128 (29), 127 (14), 115 (37), 91 (31), 77 (31), 76 (14), 65 (16), 63 (19), 51 (39).

5-Methyl-1-phenylhepta-1,3,4-triene (35): NMR (270 MHz) 7.3 (m, 5 H), 6.58 (dd, J = 15.9, 9.9 Hz, 1 H), 6.44 (d, J = 15.9 Hz, 1 H), 5.95 (dm, J = 9.9 Hz, 1 H), 2.16 (dq, J = 7.5, 2.8 Hz, 2 H), 1.76 (d, J = 2.2 Hz, 3 H), 1.02 (t, J = 7.3 Hz, 3 H); IR 3075 (sh), 3050 (sh), 3020, 2955, 2910, 2860 (sh), 2840 (sh), 1962, 1590, 1490, 1440, 1360, 1070, 960, 905.

Reaction of 6a with Allenyltributylstannane. In agreement with spectroscopic data given in ref 3b, the reaction yielded a mixture of three products: 1-phenyl-5-methylocta-1,3,4-trien-7-yne (**36c**) (in ref 3b this compound was erroniously assigned an acetylenic structure **22a**), 4-phenylnona-1,2,5-trien-7-yne (**36a**) (3:1 ratio of *E*:*Z* isomers) (**22c** in ref 3b), and 4-phenylnona-1,7-diyn-5-ene (**36b**) (**22b** in ref 3b, 3:1 ratio of *E*:*Z* isomers), at a ratio of 80:9:11, respectively.

The products were hydrogenated over palladium catalyst yielding two isomers: 5-methyl-1-phenyloctane (major) and 4-phenylnonane (minor). MS of the major isomer (t_R = 7.20 min), *m/e* (relative intensity): 204 (17, M^+), 134 (2), 133 (10), 120 (2), 119 (2), 110 (2), 106 (2), 105 (6), 93 (8), 92 (100), 91 (81), 79 (3), 78 (4), 77 (3), 71 (18), 65 (7), 57 (20), 51 (2). MS of the minor isomer (t_R = 6.30 min), *m/e* (relative intensity): 204 (8, M^+), 161 (12, M – propyl), 134 (2), 133 (21, M – pentyl), 119 (4), 105 (9), 104 (4), 92 (8), 91 (100), 78 (2), 77 (2), 65 (3).

Reaction of 6a with Tetraallylstannane. In agreement with spectroscopic data given in ref 3b, the reaction yielded a mixture of two products: 1-phenyl-5-methylocta-1,3,4,7-tetraene (**37b**) (in ref 3b it was erroneously assigned an acetylenic structure **25**), and 4-phenylnona-1,5-dien-7-yne (**37a**) (**26** in ref 3b, 1:3 ratio of *E*:*Z* isomers, not as reported there), in the ratio 64:36, respectively. The reaction products were hydrogenated over palladium catalyst yielding two products. MS of the major isomer (t_R = 7.20 min), *m/e* (relative intensity): 204 (14, M^+), 134 (2), 133 (9), 120 (2), 119 (2), 110 (2), 106 (2), 105 (9), 104 (5), 93 (7), 92 (100), 91 (94), 79 (4), 78 (5), 77 (5), 71 (16), 70 (2), 69 (3), 65 (13), 63 (2), 57 (20), 56 (4), 55 (12), 53 (3), 51 (5). MS of the minor isomer (t_R = 6.30 min), *m/e* (relative intensity): 204 (5, M^+), 161 (7, M – propyl), 134 (2), 133 (20, M – pentyl), 119 (3), 117 (2), 115 (3), 105 (8), 104 (5), 103 (3), 92 (7), 91 (100), 79 (2), 78 (3), 77 (5), 65 (4), 55 (6), 51 (3).

Reaction of 6b with Allyltributylstannane. Analogously to the above-described reaction, two products were obtained: 1,5-diphenylocta-1,3,4,7-tetraene (**38b**) and 1,5-diphenylocta-3,7-dien-1-yne (**38a**) (*E*:*Z* = 1:3), in the ratio 67:33, respectively. NMR of **38b** (270 MHz): 7.5–7.15 (m, 10 H), 6.68 (dd, J = 16, 8 Hz, 1 H), 6.58 (d, J = 16 Hz, 1 H), 6.4 (br d, J = 8 Hz, 1 H), 5.97 (m, 1 H), 5.26 (d, J = 17 Hz, 1 H), 5.08 (d, J = 11 Hz, 1 H), 3.28 (br d, J = 6.5 Hz, 2 H). IR of **38b** (neat): 3070, 3050, 3020, 2965 (sh), 2900, 2840 (sh), 2320 (vw), 1918, 1912, 1635, 1590, 1490, 1445, 1440 (sh), 1435 (sh), 1430 (sh), 1070, 1025, 985. NMR of **38a-Z** (270 MHz): 7.5–7.15 (m, 10 H), 6.08 (t, J = 10 Hz, 1 H), 5.97 (m, 1 H), 5.74 (d, J = 10 Hz, 1 H), 5.2 (d, J = 17 Hz, 1 H), 5.08 (d, J = 11 Hz, 1 H), 4.15 (br q, J = 9 Hz, 1 H), 2.56 (m, 2 H). NMR of **38a-E** (270 MHz) (partial spectrum): 7.5–7.15 (m, 10 H), 5.97 (m, 1 H), 5.07 (d, J = 17 Hz, 1 H), 5.00 (d, J = 11 Hz, 1 H), 3.36 (br q, J = 7 Hz, 1 H), 2.56 (m, 2 H).

General Procedure for Reactions with Organocopper Reagents. Reactions with Lithium Dimethylcuprate. Methyllithium (6.7 mL of 1.5 M solution in ether) was added to a stirred mixture of cuprous iodide (0.95 g, 5 mmol) in 5 mL of ether at 0 °C and the resulting solution was stirred at 0 °C for 30 min. A solution of the substrate (1 mmol) in 2 mL of ether was added and the mixture was stirred at room temperature until the reaction was complete (monitored by TLC), usually less than 12 h. A saturated aqueous solution of ammonium chloride was added, the mixture was dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography with hexane. Products ratio was determined by ^1H NMR (270 MHz).

Reactions with Lithium Alkylcyanocuprate. The reactions were carried out as described above except the organocopper reagent was prepared from 5 mmol of methyllithium (or butyllithium) and 5 mmol of cuprous cyanide.

***cis*-2-Phenylhept-3-en-5-yne (39, entry 3)**: NMR (270 MHz) 7.3 (m, 5 H), 5.89 (t, J = 6.5 Hz, 1 H), 5.42 (dq, J = 6.5, 2.0 Hz, 1 H), 4.10 (dq, J = 6.5, 7.5 Hz, 1 H), 2.00 (d, J = 2.0 Hz, 3 H), 1.38 (d, J = 7.5 Hz, 3 H).

***cis*-1,5-Diphenylhex-3-en-1-yne (39, entry 4)**: NMR (270 MHz) 7.5–7.1 (m, 10 H), 6.02 (t, J = 10 Hz, 1 H), 5.66 (d, J = 10 Hz, 1 H), 4.20 (dq, J = 10, 7 Hz, 1 H), 1.43 (d, J = 7 Hz, 3 H); IR (neat) 3080, 3060, 3030, 2960, 2930, 2880, 2320, 1600, 1500, 1450, 1370, 1230, 1220, 1070, 1030, 970, 920, 770, 710; MS, *m/e* (relative intensity) 232 (49, M^+), 217 (61), 216 (21), 215 (38), 202 (37), 155 (15), 141 (20), 128 (24), 115 (100), 108 (63), 103 (19), 102 (21), 101 (26), 95 (31), 91 (87), 89 (30), 77 (78), 65 (36), 63 (50), 51 (92).

***cis*-6-Phenyldec-2-yn-4-ene (39, entry 5)**: NMR (270 MHz) 7.2 (m, 5 H), 5.87 (t, J = 10.8 Hz, 1 H), 5.42 (dq, J = 10.8, 2.1 Hz, 1 H), 3.89 (dt, J = 10.8, 7.5 Hz, 1 H), 2.00 (d, J = 2.1 Hz, 3 H), 1.72 (m, 2 H), 1.30 (m, 4 H), 0.89 (t, J = 7 Hz, 3 H); IR (neat) 3070, 3050, 3020, 2950, 2920, 2850, 2210, 1590, 1490, 1460, 1445, 1370, 1265, 1260; MS (t_R = 8.5 min), *m/e* (relative intensity) 212 (11, M^+), 169 (6), 156 (13), 155 (100), 154 (15), 153 (21), 141 (11), 129 (15), 128 (16), 115 (29), 91 (27), 77 (23).

1-Phenyl-3-methylhex-1-en-4-yne (40, entry 1): NMR (270 MHz) 7.3 (m, 5 H), 6.60 (d, J = 16 Hz, 1 H), 6.10 (dd, J = 16, 6 Hz, 1 H), 3.28 (m, 1 H), 1.86 (d, J = 2.0 Hz, 3 H), 1.31 (d, J = 6.5 Hz, 3 H).

1-Phenyl-3-butylhex-1-en-4-yne (40, entry 5): NMR (270 MHz) 7.2 (m, 5 H), 6.58 (br d, 16.0 Hz, 1 H), 6.11 (dd, J = 16.0, 7.0 Hz, 1 H), 3.15 (m, 1 H), 1.86 (d, J = 2.4 Hz, 3 H), 1.57 (m, 2 H), 1.30 (m, 4 H), 0.89 (t, J = 7 Hz, 3 H); MS (t_R = 9.4 min), m/e (relative intensity) 212 (6, M^+), 170 (46), 155 (47), 141 (17), 129 (14), 128 (18), 115 (21), 91 (100), 77 (21).

1-Phenyl-5-methylnona-1,3,4-triene (41, entry 5): NMR (270 MHz) 7.35-7.15 (m, 5 H); 6.57 (dd, J = 16.0, 9.4 Hz, 1 H), 6.43 (d, J = 16.0 Hz, 1 H), 5.89 (dq, J = 11.9, 2.7 Hz, 1 H), 2.01 (tm, J = 8 Hz, 2 H), 1.75 (d, J = 2.7 Hz, 3 H), 1.39 (m, 4 H), 0.91 (t, J = 7.4 Hz, 3 H); IR (methylene chloride) 3070, 3030, 3005, 2950, 2920, 2860, 2845, 1935, 1620, 1590, 1490, 1440, 1360, 1260; MS (t_R = 7.5 min), m/e (relative intensity) 212 (23, M^+), 169 (5), 156 (14), 155 (100), 154 (15), 153 (22), 141 (9), 129 (15), 128 (14), 115 (29), 91 (27), 77 (20).

1,3-Diphenylpenta-1,3,4-triene (42): NMR (80 MHz) 7.3 (m, 10 H), 6.07 (d, J = 16.2 Hz, 1 H), 5.63 (d, J = 16.3 Hz, 1 H), 4.86 (d, J = 6.5 Hz, 1 H), 4.44 (d, J = 6.0 Hz, 1 H); IR (chloroform) 3070 (sh), 3050, 3020, 2920 (w), 2345, 1940 (br w), 1800 (br w), 1720 (br w), 1590, 1490, 1450, 1440, 1077, 1070, 1030, 910 (br).

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Polymer-Supported Reagents. 4.[1] Oxidation of Alcohols by Complex Chromates, Soluble Models and Supported Species[2]

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In the presence of quaternary ammonium species, chromium trioxide gave complex chromate salts $X(CrO_3)_n^-Q^+$ which were soluble in methylene chloride. These new compounds could be used as such for the oxidation of several alcohols but better efficiency was found under solid-liquid phase-transfer catalysis. Some of these complex chromates were fixed onto pyridinium and quaternary ammonium resins to give reactive polymers which were convenient in the oxidation of alcohols. The loading of the resins was achieved by an original solid-liquid-solid transfer process using quaternary ammonium salts as catalysts.

An increasing number of polymeric reagents have been designed to provide interesting facilities in organic syntheses,[3,4] one of them being the easier separation of the products from the reaction mixture.

Most of these reagents are involved in a one-step process leading to a discrete chemical modification of a substrate in solution; as the excess of reagent and spent reagent remains on the polymer, the workup is greatly facilitated. By percolating a substrate through a series of different polymeric reagents, it is possible to follow a sequence of chemical modifications to obtain the desired molecule (cascade reactions).[5]

Oxidation of alcohols to the parent carbonyl compounds is achieved by a lot of reagents,[6] though the general problem cannot be considered as definitely settled, particularly when using Cr(VI) derivatives,[7] since the workup of the reaction mixture is sometimes complicated.

Chromium trioxide is the most widely used starting material to prepare Cr(VI) oxidizing reagents by com-

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