Table I. KO_2 Reaction with *N*-Chloramines

	Amine (1)	Product (3)	% yield
a	Diisobutylamine	$(CH_3)_2CHCH{=}NCH_2CH(CH_3)_2$	88^a
b	Di-*n*-pentylamine	$CH_3(CH_2)_3CH{=}N(CH_2)_4CH_3$	73^b
c	Di-2-methylbutylamine	$EtCHCH_3CH{=}NCH_2CHCH_3Et$	71^b
d	Dibenzylamine	$PhCH{=}NCH_2Ph$	77^b
e	*N*-Ethylcyclohexylamine	$C_6H_{10}{=}NCH_2CH_3$	40^b
f		$C_6H_{11}N{=}CHCH_3$	23^b
g	*N*-Methylbutylamine	$CH_3(CH_2)_2CH{=}NCH_3$	76^b
h		$CH_3(CH_2)_3N{=}CH_2$	Trace^b
i	*n*-Hexylamine	$CH_3(CH_2)_4CH{=}NH$	49^b

[a] VPC yield of aldimine; see ref 6. [b] Isolated as 2,4-dinitrophenylhydrazone; see ref 7.

In an attempt to elucidate the mechanism we considered the possibility of a base-catalyzed reaction similar to Bachmann's.[2] However, KO_2 is no more basic than potassium acetate[8] and potassium acetate gave no imine when reacted under conditions used with KO_2. Using Na_2O_2 under these conditions, peroxide ion, a suspected product[9] of the reaction of KO_2 with *N*-chloramines, also gave no imine. When KOH was reacted with *N*-chloro-*N*-methylbutylamine, less than a 26% yield of imine was formed in the same time KO_2 gave an 82% yield. The KOH reaction was also considerably dirtier, giving several as yet unidentified products. We are therefore examining the reaction in detail for other possible intermediates.

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, and the Old Dominion University Research Foundation for the support of this research.

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(2) W. E. Bachmann, M. P. Cava, and A. S. Drieding, *J. Am. Chem. Soc.*, **76**, 5554 (1954).

(3) Thorough drying of the ether solution is required because KO_2 decomposes in the presence of water.

(4) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 330.

(5) We estimate that the crude product is >95% pure.

(6) Satisfactory elemental analysis (within 0.3%) was obtained on this compound. The yield of **3a** is based on amount of *N*-chloramine used.

(7) The structures of compounds **3b–i** were confirmed by comparison of the melting points and mixed melting points of their 2,4-dinitrophenylhydrazones with those of authentic compounds. Yields are based on amount of starting amine used.

(8) The pK_a's of the conjugate acids of superoxide and acetate are the same (4.8): see D. Behar, G. Czapski, J. Rabani, L. M. Dorfman, and H. A. Schwarz, *J. Phys. Chem.*, **74**, 3209 (1970).

(9) The white solid material at the end of the reaction appears to be a 50:50 mixture of KCl and KOOH. Acidification gave within 10% the theoretical amount of oxygen to be expected from decomposition of KOOH.

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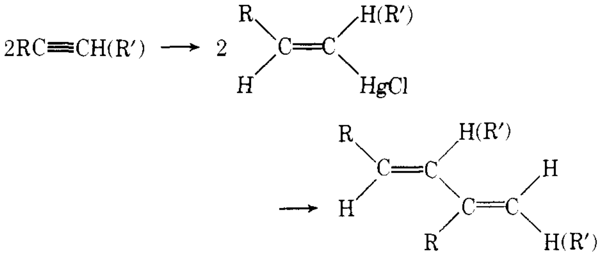
Mercury in Organic Chemistry. 15.[1] A Novel Stereospecific Synthesis of 1,3-Dienes via "Head-to-Tail" Dimerization of Alkynes

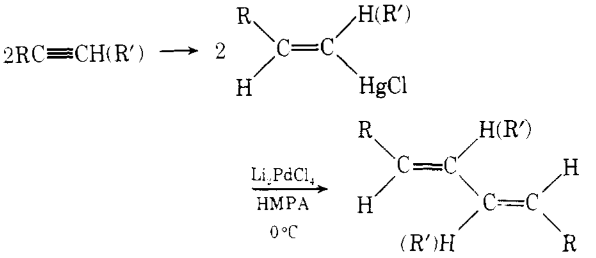
Summary: Terminal and internal alkynes can be dimerized in a "head-to-tail" fashion to provide excellent yields of unsymmetrical 1,3-dienes by preparing the corresponding vinylmercurial and treating it with palladium chloride and triethylamine in benzene at room temperature.

Sir: 1,3-Dienes have proven very valuable as intermediates in organic synthesis. Recently a number of interesting new organometallic methods have been reported for the stereospecific dimerization of terminal alkynes to 1,4-disubstituted 1,3-dienes.[2-9] For example, utilizing intermediate vinylboranes one can now prepare in a highly stereospecific manner cis,cis,[4] cis,trans,[5-7] or trans,trans[8,9] 1,4-disubstituted 1,3-dienes at will. We wish to report a novel new method employing vinylmercurials which produces unsymmetrical 1,3-dienes via "head-to-tail" dimerization of terminal and internal alkynes (eq 1).

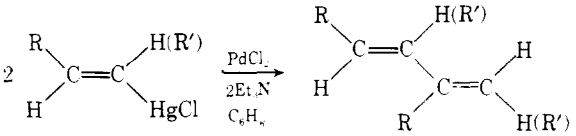


(1)

A while ago we reported a procedure for the symmetrical dimerization of vinylmercurials derived from both internal and terminal alkynes (eq 2).[10] Although the original procedure required stoichiometric amounts of lithium chloride and palladium chloride in hexamethylphosphoramide (HMPA) at 0 °C in order to obtain high yields, we have more recently found that all of the disadvantages of that procedure can be overcome by using only catalytic amounts of $[ClRh(CO)_2]_2$ to effect the dimerization.[11] Upon closer examination of the palladium reactions we have observed that "head-to-tail" dimerization can occur in these same reactions simply by varying the reaction conditions. In fact, by omitting lithium chloride and employing less polar solvents, we are able to obtain the unsymmetrical 1,3-dienes in excellent yield. Best results are obtained by using 0.5 equiv of $PdCl_2$ and employing benzene as the solvent. It was also observed that HCl is generated during the course of these reactions and the addition of triethylamine improves the yields dramatically (eq 3).



(2)



(3)

The following procedure for the synthesis of *trans*-1,3-di-*n*-butyl-1,3-butadiene is representative. *trans*-1-Hexenylmercuric chloride (10 mmol) and palladium chloride (5

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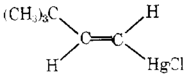
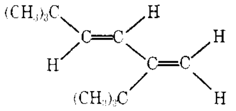
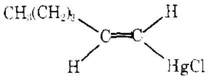
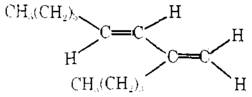
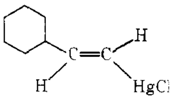
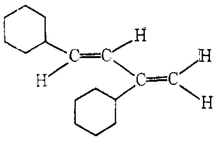
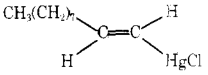
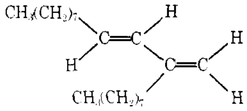
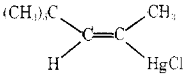
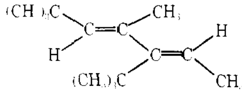
Table I. Synthesis of "Head-to-Tail" Dienes

Vinylmercurial	Diene	Time, h	Yield, %[a]
		24	91 (6)[b]
		12	98 (2) [93] (2)
		29	91 (2)
		24	[88] (5)
		16	62 (3) [59] (3)

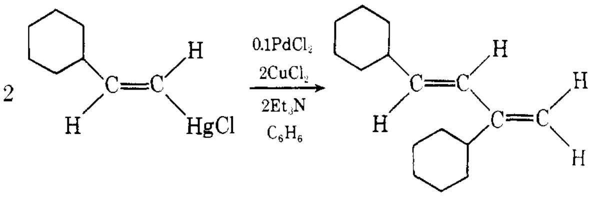
[a] GLC yield using an internal standard; [isolated yield]; (yield of symmetrical 1,3-diene impurity). [b] No triethylamine used.

mmol) were placed in a round-bottom flask under nitrogen and 100 mL of benzene was added by syringe while cooling in an ice bath. Triethylamine (10 mmol) was quickly added and the ice bath removed. The reaction was then stirred for 12 h at room temperature. Charcoal and 5 mL of saturated ammonium chloride solution were added and stirred for 15 min. The mixture was filtered and the organic layer was separated, washed with dilute acid and base, and dried. Evaporation of benzene and column chromatography (pentane) on neutral aluminum oxide provided the 1,3-diene in 93% yield (98% pure by GLC analysis): bp 73–74 °C (7 mm); MS m/e 166.1721 ± 0.8 (calcd for $C_{10}H_{22}$, 166.1722); IR (max) (CCl_4) 3090 ($=CH_2$), 3030 (*trans*-CH=CH), 1650 (diene), 1610 (diene), 965 (*trans*-CH=CH), 885 ($=CH_2$) cm^{-1}; ^1H NMR (CCl_4) δ 0.92 (t, 6 H, J = 6 Hz, CH_3's), 1.4 (m, 8 H, CH_2's), 2.1 (m, 4 H, allyl), 4.78 (br s, 2 H, $=CH_2$), 5.3–6.1 (m, 2 H, -CH=CH-). The yields and isomeric purities of other 1,3-dienes are summarized in Table I. Yields determined by GLC analysis (DC-550 or SE-30 columns) were run on one-tenth the above scale using a hydrocarbon internal standard.

Only in the synthesis of *trans*-1,3-di-*tert*-butyl-1,3-butadiene was it found advantageous to omit the triethylamine. In this case the infrared spectral data is very similar to that above and the NMR spectral data clearly exhibits a trans coupling constant of J = 16 Hz. Spectral data and analyses for all other compounds are consistent with the assigned structures.

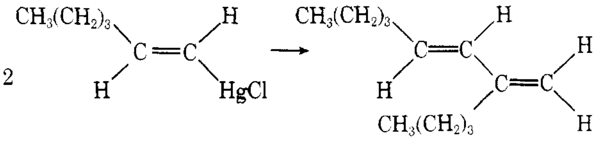
Since the reaction would achieve even greater synthetic utility were it to be effected using only catalytic amounts of palladium chloride, we have examined this possibility. Although the reaction is catalytic as run above, the catalyst turnover is generally quite low. However, addition of 2 equiv of anhydrous cupric chloride gives excellent yields using the exact procedure described above and only 10% palladium chloride (eq 4, 5).

We have also studied the analogous stoichiometric reactions of vinylalanes, -boranes, and -silanes, but only very low yields of unsymmetrical 1,3-dienes were obtained and these were contaminated by substantial amounts of the symmetrical 1,3-dienes.



(4)

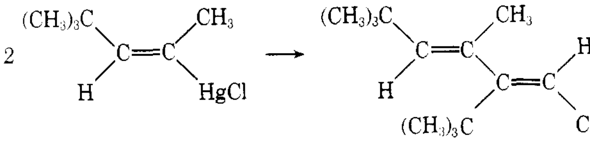
98%



(5)

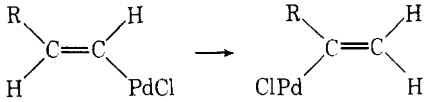
89%

The overall synthetic transformation is remarkable. The "head-to-tail" 1,3-dienes are obtained in excellent yields with only small amounts of the "head-to-head" and none of the "tail-to-tail" products. This is even true in the case of the vinylmercurial derived from 4,4-dimethyl-2-pentyne, where neither electronic nor steric effects would seem to favor formation of the "head-to-tail" diene and yet it is obtained in high purity and good yield (eq 6).



(6)

Although no totally satisfactory mechanism has yet been formulated, the reactions appear to involve palladium hydride rearrangement of an intermediate organopalladium compound (eq 7). The acid generated during the reaction quite possibly arises from decomposition of an intermediate vinylpalladium species (eq 8, 9). However, questions remain as to the role of mercury in these reactions, the driving force for rearrangement, the reason for failure to observe statistical mixtures of all three possible 1,3-dienes, and just what species is involved in the coupling reaction.



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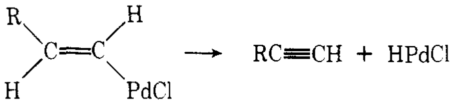

(8)

$$HPdCl \longrightarrow HCl + Pd \quad (9)$$

During the course of our investigation an apparently related process for the "head-to-tail" dimerization of terminal alkynes was reported.[12] Although the combination triisobutylalane and bis(N-methylsalicylaldimine)nickel(II) directly dimerizes terminal alkynes, the yields are generally low and numerous side products are observed. It seems likely that this reaction involves nickel hydride promoted coupling in a manner analogous to our palladium reactions.

In conclusion, both terminal and internal alkynes can be dimerized in a "head-to-tail" fashion by preparing the corresponding vinylmercurial[13,14] and treating it with palladium chloride and triethylamine in benzene at room temperature. This reaction can also be effected using only catalytic amounts of palladium chloride if anhydrous cupric chloride is employed as a reoxidant. Excellent yields of 1,3-dienes are obtained using either procedure. The mechanism of this remarkable transformation, however, remains obscure.

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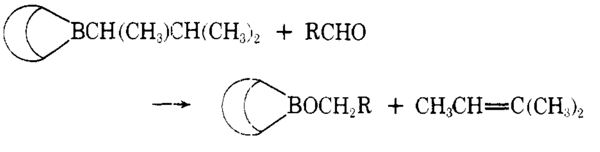
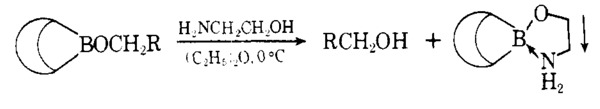
B-Alkyl-9-borabicyclo[3.3.1]nonanes as Mild, Chemoselective Reducing Agents for Aldehydes

Summary: B-Siamyl-9-BBN will reduce a variety of functionalized aldehydes to the corresponding alcohols even in the presence of unhindered ketones.

Sir: Certain *B*-alkyl-9-borabicyclo[3.3.1]nonanes (9-BBN) have been shown to be effective reducing agents for benzaldehyde. The efficiency of these compounds as reducing agents is largely dependent on the structure of the alkyl group on 9-BBN.[1] We wish to report that *B*-(3-methyl-2-butyl)-9-borabicyclo[3.3.1]nonane (*B*-siamyl-9-BBN)[2] is an effective reagent for the reduction of a wide variety of aldehydes under mild conditions.[3] The formation of an intermediate alkoxyborane is accompanied by the liberation of 2-methyl-2-butene (eq 1).[4] The boron species is conveniently removed by precipitation as the ethanolamine complex, leaving the alcohol in solution. Several representative examples of successful conversions of aldehydes are presented in Table I, which illustrates a number of attractive features of the reagent system.



(1)



(2)

Table I. Reduction of Aldehydes to Alcohols with *B*-Siamyl-9-BBN

Product^a	% yield^b
$CH_3(CH_2)_4CH_2OH$	103 (54)
$(CH_3)_3CCH_2OH$	101 (49)
$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OH^c$	100 (76)
$C_6H_5CH{=}CHCH_2OH^d$	82 (62)
$C_6H_5CH_2OH$	97 (90)
p-$ClC_6H_4CH_2OH$	92 (80)
p-$CH_3OC_6H_4CH_2OH$	97 (65)
p-$(CH_3)_2NC_6H_4CH_2OH$	(92)
p-$O_2NC_6H_4CH_2OH$	(76)

^{a} All compounds exhibited satisfactory spectra in accord with the assigned structure. ^{b} Determined by GLC using calibrated internal standard, numbers in parentheses indicate isolated yields. ^{c} A mixture of 61% geranial and 39% neral; the same ratio of geraniol and nerol was obtained. ^{d} *trans*-Cinnamaldehyde; the product had spectral properties identical with those of *trans*-cinnamyl alcohol.

First, trialkylboranes are exceedingly tolerant of many functional groups.[5] For example, *B*-siamyl-9-BBN reduces α,β-unsaturated aldehydes to allylic alcohols with neither detectable conjugate reduction nor 1,4 addition of the alkylborane in the absence of oxygen.[6] Branched or highly hindered aliphatic aldehydes are reduced almost as rapidly as straight-chain aldehydes; hexanal is reduced only slightly faster than pivalaldehyde. The rate of reduction of para-substituted benzaldehydes is increased by electron-withdrawing groups and decreased by electron-donating groups. Benzaldehyde is reduced about ten times faster than *p*-dimethylaminobenzaldehyde.

Perhaps the most remarkable feature of the *B*-alkyl-9-BBN compounds is their ability to selectively reduce aldehydes in the presence of ketones. While a number of reagents[7] have been devised which show similar discrimination, only diisopropyl carbinol on alumina is reported to be sufficiently selective to reduce an aldehyde in preference to an unhindered cyclohexanone.[7g] We have found that substantial reduction of a wide variety of ketones is attained only after many days at reflux with *B*-siamyl-9-BBN.[8] Cyclohexanone itself is reduced only to the extent of 2–3% under conditions for aldehyde reduction. Indeed, a competition between benzaldehyde and acetophenone for a single equivalent of *B*-siamyl-9-BBN resulted in a >95% reduction of the aldehyde in 2 h with no detectable reduction of the ketone.[9]

Two substrates, *p*-dimethylaminobenzaldehyde and *p*-nitrobenzaldehyde, proved troublesome since the intermediate alkoxyborane could not be subjected to the usual workup conditions without incurring decomposition. Modified procedures for these allowed isolation of the alcohols with no further complications.

A general procedure for aldehyde reduction is as follows. A dry, 200-mL flask with a side arm covered by a rubber septum, containing a magnetic stirring bar, and surmounted by a reflux condensor connected to a mercury bubbler, was flushed with nitrogen. To the flask was added 62 mL of a 0.5 M solution of 9-BBN in THF (31 mmol), followed by 3.4 mL of distilled 2-methyl-2-butene (32 mmol). The mixture was stirred at reflux for 2 h. Then 30 mmol of freshly distilled aldehyde was injected into the flask.[10,11] Solid aldehydes were first dissolved in a small volume of THF and the solution was introduced into the reaction vessel via syringe. At the end of 2 h of reflux the solution was cooled to room temperature. Then ~0.2 mL of acetaldehyde was injected into the flask to destroy excess organoborane and the solution was stirred for 15 min. The solvent and volatile components were removed

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