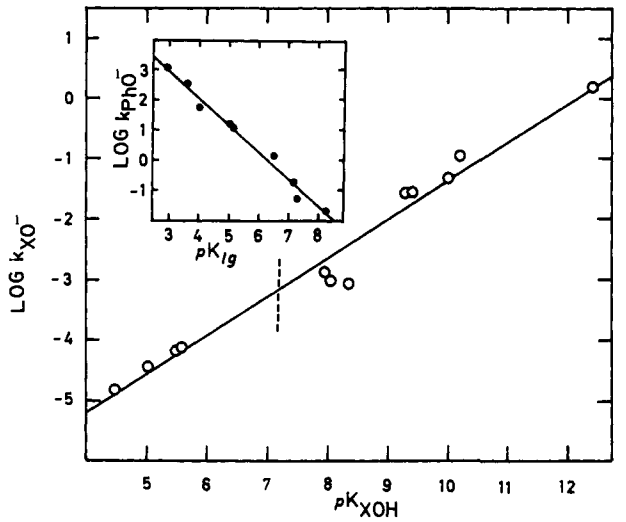

Figure 1. Reaction of oxyanions with 4-nitrophenyl 4-nitrobenzenesulfonate (○). Nucleophiles in increasing order of pK: acetate, succinate, dianion, pentafluorophenolate, 2,3,5,6-tetrafluorophenolate, 4-cyanophenolate, 4-acetylphenolate, 3,4,5-trichlorophenolate, hexafluoroisopropoxide, 4-chlorophenolate, phenolate, 4-methoxyphenolate, and trifluoroethoxide. Inset: Reaction of phenolate ion with substituted phenyl esters of 4-nitrobenzenesulfonic acid (●). Phenol leaving groups in ascending order of pK: 4-chloro-2,6-dinitro, 2,6-dinitro, 2,4-dinitro, 2,4-dichloro-6-nitro, 2,5-dinitro, 4-chloro-2-nitro, 4-nitro, 2-nitro, and 3-nitro. Conditions for the kinetics (units, M^{-1} s^{-1}): 50 °C, 10% dioxan and ionic strength made up to 0.5 M with KCl. The lines are calculated from the equations in the text and the dashed line indicates the expected breakpoint for the putative stepwise process.

The results indicate no substantial change in transition-state structure over the range of basicity represented by 8 pK units even when ΔpK's for phenols alone range well above and below zero. Since the reaction is symmetrical, the effective charge on oxygen in forming and cleaving bonds must be identical in the transition state. Reaction of phenolate ion with a series of aryl esters of 4-nitrobenzenesulfonic acid obeys a linear Brønsted-type relationship: $\log k_{PhO^-} = (-0.91 \pm 0.09)\ pK_{LG} + (5.80 \pm 0.60)$ ($r = 0.991$). No evidence is seen of a steric effect of ortho substituents (see Figure 1). The β_{EQ} for the reaction is the sum of the two β values ($\beta_{EQ} = 1.6 \pm 0.2$) obtained in this work[4] since there is only one transition state. The change in effective charge on entering and leaving oxygen (respectively +0.64 and −0.91 in a total change of 1.6) is consistent with relatively weak S–O bonds.

Martin and co-workers[5] demonstrated that the apical S–O bond lengths in pentacoordinate analogues of the putative intermediate are substantially increased over the lengths in the tetrahedral structures. This does not agree with the observation of a single transition state, although we cannot exclude the possibility that a (very reactive) pentacoordinate intermediate is formed at a very shallow well at the apex of the potential energy maximum so that the two transition states would have closely similar electronic structures. Confirmation of the concerted mechanism is not yet possible by ^{17}O,^{18}O-stereochemical labeling, but it is established that the stereochemistry of sulfur is inverted during transfer of the sulfinate group.[6] The stereochemical probe is not, however, able to distinguish a very reactive intermediate from a concerted mechanism.

These results must not be taken to imply that *all* sulfonyl-transfer reactions are concerted. There is evidence that an intramolecular reaction could be stepwise.[7] It has now been conclusively established that the analogous phosphoryl transfer can be *either* concerted *or* stepwise.[8,9]

The reactions were followed by observing the increase in absorbance at 400 nm. Second-order rate constants were obtained from the slope of plots of values of k_{obsd} against the concentration of the nucleophile in the range 0–0.2 M; the increase in k_{obsd} was always substantially in excess of 100%, and the derived second-order rate constants were independent of added buffer. The reactions were demonstrated to involve nucleophilic attack by the oxyanion rather than general base catalyzed hydrolysis. An essentially theoretical yield of the phenyl ester was obtained when the 4-nitrophenyl ester was reacted in the presence of phenolate buffers. A negligible deuterium oxide solvent isotope effect was seen with acetate reacting with the 4-nitrophenyl ester ($k_{AcO}^{H_2O}/k_{AcO}^{D_2O} = 0.93$). Reaction of hindered reagents (2,2-diethylmalonate-dianion and 2,4,6-collidine) with the 4-nitrophenyl ester gave reactivities at least an order of magnitude below that calculated from the equation.

Registry No. 4-Nitrophenyl 4-nitrobenzenesulfonate, 30362-87-9; acetate, 71-50-1; succinate dianion, 56-14-1; pentafluorophenolate, 26910-95-2; 2,3,5,6-tetrafluorophenolate, 91178-72-2; 4-cyanophenolate, 14609-76-8; 4-acetylphenolate, 18983-84-1; 3,4,5-trichlorophenolate, 60154-34-9; hexafluoroisopropoxide, 44870-01-1; 4-chlorophenolate, 24573-38-4; phenolate, 3229-70-7; 4-methoxyphenolate, 29368-59-0; trifluoroethoxide, 24265-37-0; 4-chloro-2,6-dinitrophenol, 88-87-9; 2,6-dinitrophenol, 573-56-8; 2,4-dinitrophenol, 51-28-5; 2,4-dichloro-6-nitrophenol, 609-89-2; 2,5-dinitrophenol, 329-71-5; 4-chloro-2-nitrophenol, 89-64-5; 4-nitrophenol, 100-02-7; 2-nitrophenol, 88-75-5; 3-nitrophenol, 554-84-7.

(4) This is close to a value obtained for a different sulfonyl-group-transfer equilibrium.[2b]

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Carbon–Carbon Bond Formation by Induced Elimination from Unsymmetrically Substituted (Allyl)(allyl')palladium Complexes

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We recently developed procedures to utilize (η^3-allylic)(η^1-alkenyl)palladium(II) intermediates in stereospecific coupling reactions in which C–C bond formation occurs by reductive elimination from diorganopalladium(II) intermediates;[1] comparable methodology could be envisaged to be applicable to the recurrent problem of allylic cross-coupling.[2] Indeed, we have now found it possible to specifically prepare *unsymmetrically* substituted (allyl)(allyl')palladium(II) complexes and to induce reductive elimination to give high yields of 1,5-dienes in which "head-to-head" coupling predominates.

The preparation of (η^3-allylic)palladium(II) halide complexes from olefins is well documented,[3] as is the reaction between various metal salts and allylic metallic species.[4] Symmetrical bis(η^3-allyl)palladium(II) species have been prepared thusly.[5] Spon-

(1) (a) Temple, J. S.; Riedeker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (b) Hayasi, Y.; Riediker, M.; Temple, J. S.; Schwartz, J. *Tetrahedron Lett.* **1981**, 2629.

(2) (a) Katzenellenbogen, J. A., Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326. (b) Stork, G.; Grieco, P. A.; Gregson, M. *Tetrahedron Lett.* **1969**, 1393. (c) Axelrod, E. H.; Milne, G. M.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1970**, *92*, 2139. (d) Biellmann, J. R.; Ducep, J. B. *Tetrahedron Lett.* **1969**, 3707. (e) Godschalx, J. P., Stille, J. K. *Ibid.* **1983**, 1905. (f) Corey, E. J.; Hegedus, L. S.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 2416. (g) van Tamelen, E. E.; Åkermark, B.; Sharpless, K. B. *Ibid.* **1969**, *91*, 1552. (h) Yamada, Y.; Momose, D.; Iguchi, K.; Sugiyama, T. *Tetrahedron Lett.* **1983**, 921. (i) Trost, B. M.; Keinan, E. *Ibid.* **1980**, 2595. (j) Godschalx, J.; Stille, J. K. *Ibid.* **1980**, 2599.

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(5) Wilke, G.; et al. *J. Organomet. Chem.* **1980**, *191*, 425.

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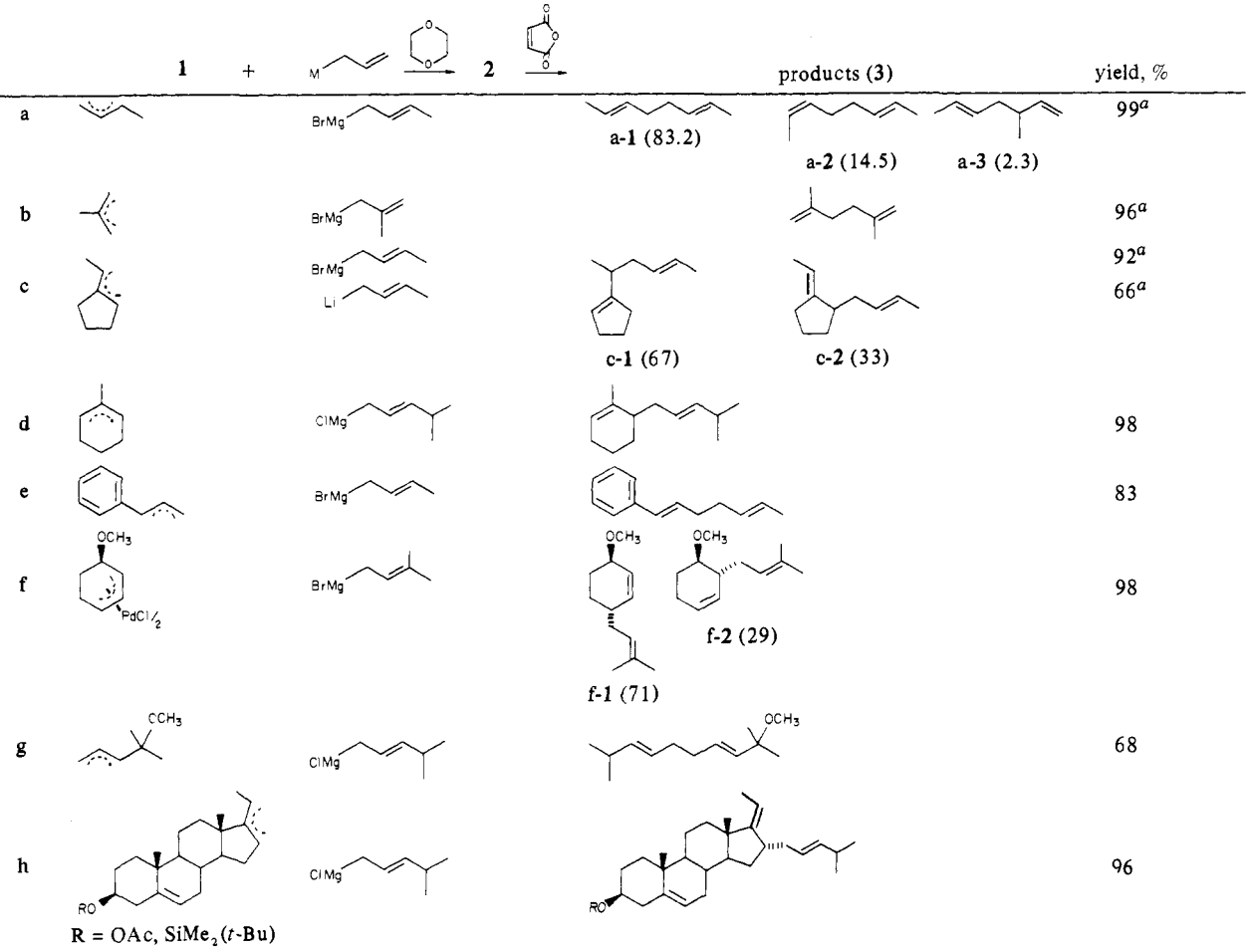
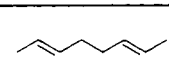
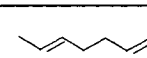
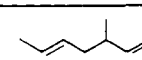
Table I. Results of Unsymmetrical Allyl-Allyl Coupling



[a] Denotes GC yields; all others are isolated yields.

Table II. Product Distribution for Oxidation of **2a**

2a $\xrightarrow{[Ox]}$ products (**3a**)

oxidant				other[a]	C_8 yield, %
Na_2IrCl_6[b]	38.1	15.1	29.4	27.2	42
$(NH_4)_2Ce(NO_3)_6$[b]	33.7	17.2	31.2	17.6	35
$CuCl_2$[b]	37.8	16.2	32.1	13.9	11
electrolysis[c]	40.6	12.4	36.7	10.2	34

[a] Unidentified C_8 material. [b] Oxidant added to MeCN solution of bis(allyl) at −30 °C. [c] Ionic medium 0.1 M Bu_4NBF_4 in MeCN; reference electrode Ag, AgCl; Pt working electrode; −30 °C.

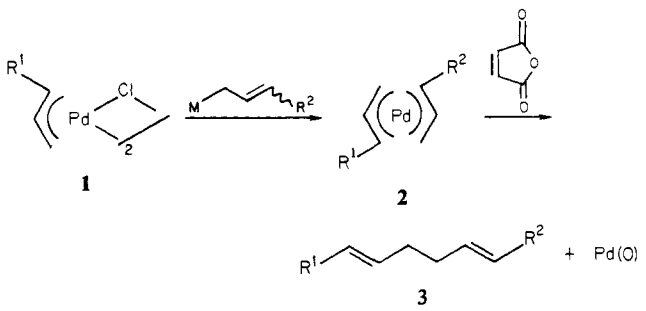
taneous reductive elimination from these complexes does not occur; alkyl group-substituted allylic complexes decompose by processes involving hydride transfers.[4] Reductive elimination of 1,4-dienes from (η^3-allyl)(η^1-alkenyl)palladium(II) species can be induced by π-acidic ligation[1] and an analogous procedure to accomplish allylic coupling was developed. Crotylmagnesium bromide (0.60 mmol, in ether) was slowly added to a suspension of crotylpalladium chloride (**1a**) (100 mg, 0.51 mmol Pd) in 10 mL of dry, air-free ether at −30 °C. The reaction mixture was stirred for 2 h, and maleic anhydride (259 mg, 2.64 mmol) dissolved in THF (2 mL) was added; the reaction mixture was stirred for an additional 2 h and then permitted to rise slowly to room temperature. The reaction mixture was filtered, and products were distilled and analyzed by gas chromatography (0.1% SP-1000 on Carbopack). Product was obtained (99.3% by GC) in a ratio of 97.7:2.3 for "head-to-head" (**3a-1,2**) vs. "head-to-tail" (**3a-3**) coupling (the head-to-head material was *E,E*, 83.2%, and *E,Z*, 14.5%).[6] In the absence of maleic anhydride only 6.6% of coupled products were obtained in a ratio of 50:31:19 for head-to-head, head-to-tail, and other unidentified C-8 materials.

The problem of *unsymmetrical* allylic coupling is more complex. Treatment of (allylic)palladium chloride (**1**) with an allylic Grignard species, under the conditions described above, gave a *mixture* of products suggesting rapid allylic ligand metathesis involving (allyl)(allyl′)palladium(II) (**2**) and magnesium salt residues. We find, though, that the presence of dioxane suppresses allylic ligand metathesis since it precipitates magnesium halide residues as adducts. In this way, a variety of nonsymmetrically substituted bis(allylic) complexes of Pd(II) could be obtained.[7] To accomplish selective cross-coupling, crotylmagnesium bromide (0.25 mmol in ether) was added to a suspension of (η^3-allylic)-palladium complex **1c** (47 mg, 0.20 mmol) in ether (5 mL) containing dioxane (51 μL, 0.60 mmol) at −30 °C (Scheme I). After 1 h maleic anhydride (98 mg, 1 mmol) was added. After an additional 2 h, the solution was allowed to warm to room

(6) Crotyl Grignard/halide coupling produces 88% head-to-tail product; see: Young, W. *J. Am. Chem. Soc.* **1945**, *67*, 841.

(7) For **2c** four isomers (syn,anti/cis,trans) may be seen by ^{1}H NMR.

Scheme I



temperature. The reaction mixture was filtered, and products were isolated in a combined yield of 92%. No coupled product was obtained in the absence of maleic anhydride in which case all of **1c** was converted to diene and olefins. Without dioxane, only 2% of cross-coupled material was obtained; the predominant products of coupling were derived from crotyl groups exclusively (Table I).

The stereochemistry of coupling was established by examination of products **3f-1** and **3f-2** prepared from (η^3-allyl)palladium complex **1f** in which the palladium moiety is trans to the methoxy substituent.[8] Compound **3f-1** was assigned a trans stereochemistry by ^{1}H NMR[8,9] as was **3f-2**. That carbon–carbon bond formation occurs on the same face of the η^3-allylic unit as that one to which the palladium was attached substantiates the notion that carbon–carbon bond formation occurs via a sequence of transmetalation and reductive elimination.[10,12]

Methods other than π-acidic ligand coordination could induce reductive elimination from **2**, and a series of oxidative procedures were therefore examined. Cyclic voltammetric analysis of bis(allyl)palladium(II) and bis(crotyl)palladium(II) showed an irreversible oxidation at −0.85 and −1.25 V (vs. SCE), respectively. Preparative electrochemical techniques or 1e$^-$ oxidants were utilized to induce elimination from bis(allylic)palladium(II) species;[13] however, low yields and selectivities of products resulted (see Table II). Significant amounts of byproduct allylic chloride and allylpalladium chloride were obtained when Na_2IrCl_6 was used as the oxidant suggesting a radical decomposition or a competition between bona fide reductive elimination and radical decomposition (the existence of radical decomposition pathways has been noted in oxidation of diorganoiron,[14] -nickel,[15] and -platinum species[16]).[17]

That complementary regiochemistries for carbon–carbon bond formation can occur for reactions between (allyl)palladium halides and other allylic metallic species, depending on the choice of a direct attack[2i,j] or a transmetalation sequence, gives the synthetic chemist a satisfactory degree of control in allylic–allylic cross-coupling sequences in which "head" and "tail" of the allylic units are sterically clearly different.

Acknowledgment. We acknowledge support for this work given by the National Institutes of Health and the National Science Foundation.

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(9) Stereochemical assignments were made by a series of decoupling and NOE experiments; for the protons on methoxy-substituted carbon and on the adjacent methylene carbon, for **3f-1** J = 8.4 Hz and for **3f-2** J = 8.9 Hz.

(10) Selective attachment at C(20) occurs in maleic anhydride induced coupling between a steroid-derived (η^3-allylic)palladium complex and an *alkenyl*zirconium reagent.[1a] An analogous procedure using an *allylic* Grignard gave coupling almost exclusively at C(16) with side-chain attachment determined to be α by ^{13}C and ^{1}H NMR comparison with authentic material; for the C(20) coupled product, the *R* configuration was obtained. Thus, in both cases, product is formed by transmetalation–reductive elimination. This change in coupling selectivity may be due to a fixed (η^3-allylic)palladium-(η^1-alkenyl) configuration in the first case,[1a] a geometrically labile bis(allylic)palladium complex[11] in the latter, and the possible existence of competing direct and conjugate coupling mechanisms for bis(allylic)palladium species.

(11) A number of syn–anti isomers are possible. As well, for **2b**, ^{1}H NMR analysis suggests the presence of an (η^3-allyl)(η^1-allyl) isomer: at −60 °C δ (CD_2Cl_2) 4.75–5.20 (m, 2 H), 1.78 (br s, 3 H), 1.06 (d, d, 2 H).

(12) Other π-acidic ligands (e.g., fumaronitrile or benzoquinone) were also successfully employed.

(13) Both discrete **2** and $P(CH_3)_3$ adducts of **2** (to give an η^3, η^1, PMe_3 species) were utilized. Low-temperature NMR of the latter was identical with that reported: Wilke, G.; et al. *J. Organomet. Chem.* **1980**, *191*, 449.

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(15) Almemark, M.; Åkermark, B. *J. Chem. Soc., Chem. Commun.* **1978**, 66.

(16) Chen, J. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 1450.

(17) The presence of the free radicals was further substantiated by their being trapped by O_2.

Stereoselective Aminoacylation of Polyribonucleotides

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Contemporary proteins contain only L-amino acids, and nucleic acids contain only D nucleosides, but the pathway for the coevolution of the chirality of these molecules is unknown. With present-day aminoacyl-tRNA synthases the L-amino acid generally is linked to the 3′ end of the tRNA molecule more rapidly than the D isomer,[1] but simple *chemical* aminoacylation at the 3′-terminus of a dinucleoside monophosphate was found to be chirally nonselective.[2] Thus the observation of chiral selection in a nonenzymatic reaction that yields aminoacyl esters of RNA may be of potential importance for reconstructing the evolution of this chiral specificity.

We now report that the reaction of racemic [*N*-(3,5-dinitrobenzoyl)-DL-alanyl]imidazole with D-poly(adenylic acid) (poly(A)), poly(uridylic acid) (poly(U)), poly(cytidylic acid) (poly(C)), or poly(inosinic acid) (poly(I)) resulted in the preferential acylation of each polynucleotide by the L enantiomer of *N*-(3,5-dinitrobenzoyl)alanine. The stereoselective reaction appeared to take place on the "internal" 2′-hydroxyl groups, and the enantiomeric excess (ee) was usually 40–60%.

Polynucleotides were purchased from P-L Biochemicals and dialyzed for 2 days against 10 mM tris(hydroxymethyl)aminomethane buffer (pH 7.0) containing 1 mM ethylenediaminetetraacetic acid and then against 10 mM triethylammonium bicarbonate (pH 8.1). *N*-(3,5-Dinitrobenzoyl)-DL-alanine was prepared by the Schotten–Baumann procedure of Ronwin.[3] To form a 0.3 M solution of the imidazolide, this amino acid (10.3 mg, 36 μmol) was dissolved in 0.125 mL of dimethylformamide (DMF), 1,1′-carbonyldiimidazole (6.3 mg, 39 μmol) was added, and the solution was incubated for 30 min at room temperature.[4] A 0.6 M solution of the imidazolide in DMF was prepared similarly. The acylation of polynucleotides by both 5 and 10 equiv of imidazolide per nucleoside hydroxyl group was studied. The polymer (1.5 μmol in nucleoside units) in 75 μL of H_2O was treated with 25 μL of either the 0.3 or 0.6 M imidazolide solution. After a 1-h incubation at room temperature, the reaction mixture was applied to a 1.1 × 23.5 cm Bio-Gel P2 column (Bio-Rad Laboratories) and eluted with 0.1 M triethylammonium acetate (pH 6.4). The absorbance of the eluate was monitored at 248.5 nm, and the well-resolved fraction corresponding to the acylated polynucleotide was isolated and lyophilized. Each acylated polymer was treated with 0.1 N NaOH (1 h, room temperature), and the liberated *N*-(3,5-dinitrobenzoyl)-DL-alanine was purified by HPLC on an octadecylsilyl bonded-phase column using a 0.1 M ammonium acetate buffer (pH 4.7) and an acetonitrile gra-

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(2) Profy, A. T.; Usher, D. A. *J. Mol. Evol.* **1984**, *20*, 147–156. However, the equilibrium constant for the 2′ ⇌ 3′ aminoacyl migration reaction in inosinylylinosine does differ for D- and L-Boc-alanine.

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