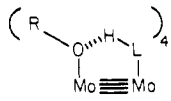
Table I. Comparison of M-M, M-O, and M-N/P Distances in Some Dimolybdenum (M≡M) and (M≣M) Compounds Supported by O, N, and P Donor Ligands

compound[a]	M-M bond order	M-M, Å	M-O, Å (av)	M-N/P, Å (av)	ref
$Mo_2(OCH_2$-t-$Bu)_6$	3	2.222 (2)	1.88 (1)		*b*
$Mo_2(O$-i-$Pr)_6(py)_2$	3	2.250 (2)	1.93 (1)	2.32 (1)	*c*
$Mo_2(O$-i-$Pr)_4(mhp)_2$	3	2.206 (1)	1.91 (1) OR, 2.04 (1) mhp	2.27 (1)	*d*
$Mo_2(O$-i-$Pr)_4(py)_4$	4	2.195 (1)	2.03 (1)	2.27 (1)	*e*
$Mo_2(OCH_2$-t-$Bu)_4(PMe_3)_4$	4	2.209 (1)	2.03 (2)	2.54 (2)	*e*
$Mo_2(mhp)_4$	4	2.065 (1)	2.09 (1)	2.17 (1)	*f*
$Mo_2(OCH_2$-t-$Bu)_4(HNMe_2)_4$	4	2.133 (2)	2.08 (1)	2.27 (2)	*e*
$Mo_2(O$-i-$Pr)_4(HO$-i-$Pr)_4$	4	2.110 (3)	2.09 (1) OR, 2.17 (1) HOR		*e*
$Mo_2(O_2CMe)_4$	4	2.093 (1)	2.11 (2)		*g*

[a] mhp is the anion of 2-hydroxy-6-methylpyridine; py = pyridine. [b] Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* 1977, *16*, 1801. [c] Leonelli, J. Ph.D. Thesis, Indiana University, 1982. [d] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Inorg. Chem.* 1981, *20*, 2215. [e] This work. [f] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* 1978, *100*, 4725. [g] Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr., Sect. B* 1974, *B30*, 2768.

Pr)$_4$(py)$_4$, and $Mo_2(O$-i-$Pr)_4(HO$-i-$Pr)_4$ with those for some related $(Mo{\equiv}Mo)^{6+}$ and $(Mo\overset{4}{-}Mo)^{4+}$ containing compounds is given in Table I. The following points are worthy of note: (1) The Mo–Mo distances in $Mo_2(OCH_2$-t-$Bu)_4(PMe_3)_4$ (2.209 (2) Å) and $Mo_2(O$-i-$Pr)_4(py)_4$ (2.196 (1) Å) are the longest reported for Mo–Mo quadruple bonds. (2) The Mo–OR distances in the $(Mo\overset{4}{-}Mo)^{4+}$ containing compounds are more than 0.1 Å longer than those found in $(Mo{\equiv}Mo)^{6+}$ containing compounds. (3) The compounds $Mo_2(OR)_4L_4(M\overset{4}{-}M)$, where L = $HNMe_2$ and *i*-PrOH, contain hydrogen bonds across the Mo–Mo bond of the type depicted by II.[5] This results in (i) a shorter Mo–Mo distance,



II

(ii) longer Mo–OR distances, and (iii) smaller RO–Mo–Mo angles, relative to the $Mo_2(OR)_4L_4$ compounds where L = py and PMe_3.[6]

Qualitatively, these structural features may be understood in terms of the mutual influence of the alkoxide π-donor ligand and the Mo–Mo quadruple bond. In the $(Mo{\equiv}Mo)^{6+}$ containing compounds, either one or both of the in-plane Mo atomic orbitals ($d_{x^2-y^2}$, d_{xy}) are available for RO-to-Mo π-bond formation. In $(Mo\overset{4}{-}Mo)^{4+}$ containing compounds, there are formally no vacant Mo d atomic orbitals to form π-bonds with the RO ligands. Four d orbitals are used to form the Mo–Mo quadruple bond, $\sigma^2\pi^4\delta^2$ (d_{z^2}, d_{xz}, d_{yz}, and d_{xy}), and one ($d_{x^2-y^2}$) is used in combination with s, p_x, and p_y to form Mo–OR/L σ-bonds. The filled oxygen p atomic orbitals will mix with the empty Mo–Mo δ^* and π^* molecular orbitals, thereby weakening and lengthening the Mo–Mo bond. The introduction of hydrogen bonds across the Mo–Mo bond, as shown in II, serves to neutralize the π-donor properties of the RO ligand, thus lengthening and shortening the Mo–OR and Mo–Mo distances, respectively.

Both the reactivity patterns and the physicochemical properties of these new compounds of type I are under investigation.[7]

Supplementary Material Available: Listings of atomic positional parameters for $Mo_2(O$-i-$Pr)_4(py)_4$, $Mo_2(O$-i-$Pr)_4(HO$-i-$Pr)_4$, $Mo_2(OCH_2$-t-$Bu)_4(PMe_3)_4$, and $Mo_2(OCH_2$-t-$Bu)_4(HNMe_2)_4$ (4 pages). Ordering information is given on any current masthead page.

(7) We thank the Department of Energy, Office of Basic Chemical Sciences, and the Wrubel Computing Center for support.

(5) This type of RO---HOR bonding was seen in $W_2Cl_4(OR)_4(HOR)_2$ compounds and has been noted to give rise to both symmetric and asymmetric hydrogen bridges: Cotton, F. A.; Falvello, L. R.; Fredrick, M. F.; DeMarco, D.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 3088. In the present case the bridging hydrogens were located in the Fourier difference map for $Mo_2(OCH_2$-t-$Bu)_4(HNMe_2)_4$ but not for $Mo_2(O$-i-$Pr)_4(HO$-i-$Pr)_4$. In the ^{1}H NMR spectra the bridging hydrogen appears at low field consistent with its position over the M–M multiple bond: $Mo_2(O$-i-$Pr)_4(HO$-i-$Pr)_4$ δ(OH–O) = 13.1 ppm and $Mo_2(OCH_2$-t-$Bu)_4(HNMe_2)_4$ δ(O–HN) = 6.9 ppm.

(6) Compare Mo–Mo–O angles (averaged) in $Mo_2(OCH_2$-t-$Bu)_4L_4$ which are 101° and 110° when L = $HNMe_2$ and PMe_3, respectively.

Asymmetric Acylation Reactions of Chiral Imide Enolates. The First Direct Approach to the Construction of Chiral β-Dicarbonyl Synthons[1]

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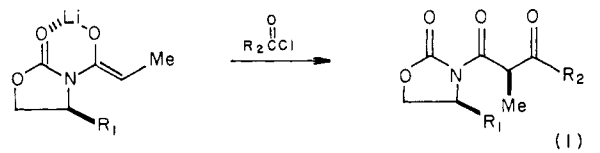
In conjuction with our general interest in the development of chiral enolate systems derived from oxazolidone imides,[3] we recently made the striking observation that these enolates undergo highly diastereoselective acylation reactions (eq 1). Although



(1)

conventional wisdom suggests that the integrity of the newly created asymmetric center in these β-dicarbonyl adducts might be readily lost via enolization, we have found that this has not

(1) Presented at the 182nd National Meeting of the American Chemical Society, New York, NY, Aug 27, 1981.

(2) Present address: Department of Chemistry, Harvard University, Cambridge, MA 02138.

(3) (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *Ibid.* **1982**, *104*, 1737. (c) Evans, D. A. *Aldrichimica Acta* **1982**, *15*, 23.

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Table I. Stereoselective Acylation Reactions of Imides **1** and **2** (Scheme I)

entry	imide	acid chloride	kinetic ratio (3:4)[a]	isolated yield, %[b]	$[\alpha]_{589}$ (*c*, CH_2Cl_2), deg	mp, °C
A	**1**	EtCOCl	96:4	88 (**3a**, R = Et)	−17.2 (2.5)	131–132
B	**2**	EtCOCl	5:95	83 (**4b**, R = Et)	+108.3 (1.4)	123–124
C	**1**	PhCOCl	96:4	93 (**3a**, R = Ph)	−62.3 (0.3)	oil
D	**2**	PhCOCl	5.5:95.5	92 (**4b**, R = Ph)	+154.5 (0.52)	164.5–165
E	**1**	MeCOCl	96:4	95 (**3a**, R = Me)	−22.8 (1.4)	134–135
F	**2**	MeCOCl	30:70	55 (**4b**, R = Me)	+111.9 (1.20)	116.5–117.5

[a] Ratios determined by HPLC.[8] [b] Diastereomer purity 99%. Entry C purified by chromatography.[7] All other examples purified by recrystallization.

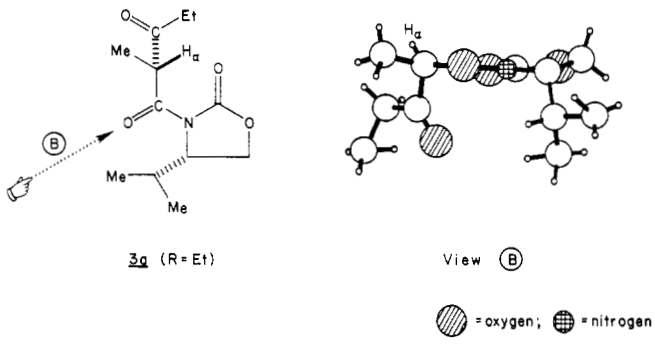
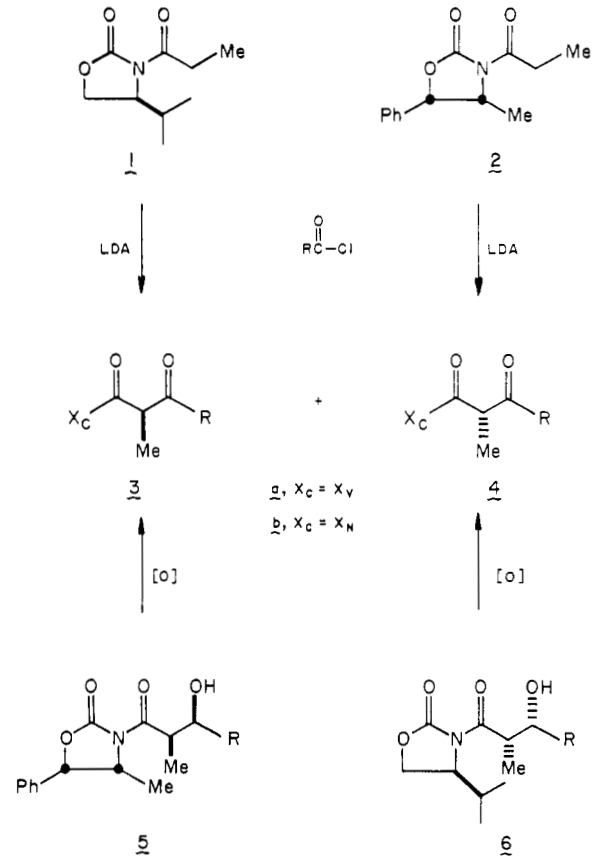


Figure 1. X-ray structure of **3a** (R = Et).

been the case. The purpose of this communication is to disclose our observations in this area.

In the present study the chiral propionimides **1** and **2**[3a] were transformed into their respective *Z* lithium enolates with lithium diisopropylamide (LDA) under previously described conditions.[3b] Cannulation[4] of a 0.5–1.0 molar solution of enolate in THF (−78 °C) into a cooled (−78 °C) 0.5–1.0 molar THF solution of acid chloride (1.1 equiv) followed by an immediate quench with a saturated solution of aqueous ammonium chloride afforded the desired β-keto imides **3** and **4** after a conventional isolation procedure.[5,6] Minor diastereomer impurities were removed by either recrystallization or chromatography.[7] In all of the cases documented in Table I, these purification techniques readily afforded diastereomerically pure (≥99%) β-keto imides.[8,9] In all but one case (entry F), enolate acylation exhibited kinetic reaction diastereoselection at the 95% level. In these reactions, the sense of asymmetric induction may be projected from the chelated *Z* lithium enolate illustrated in eq 1 wherein enolate π-facial selection is dictated by transition state steric effects imposed by the R_1 subsitutent. An unequivocal stereochemical assignment of β-keto imide **3a** (R = Et)[6] was gained from its X-ray structure, two views of which are illustrated in Figure 1. Further stereochemical correlations relevant to this study were made by oxidation of the previously synthesized β-hydroxy imides **5** and **6** (R = Me, Et, Ph) (cf. Scheme I).[3a] The method of choice for this operation proved to be the modified Moffatt procedure using Me_2SO–SO_3·py (py = pyridine) complex.[10,11] In a typical experiment, the β-hydroxy imide **6** (R = Ph) was oxidized in 90% yield to **4a** (R = Ph), mp 167–167.5 °C, with ≤1% epimerization

Scheme I

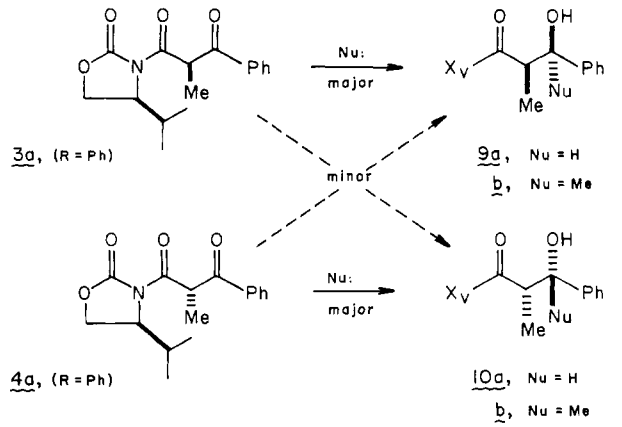


at the methyl-bearing stereocenter.[6] This protocol for the independent synthesis of each of the *minor* diastereomeric acylation products allowed for their independent characterization and stereochemical correlation.

The low kinetic acidity exhibited by the β-keto imides **3** and **4** is quite striking. For example, both **3** and **4** are quite stable to silica gel chromatography and other acidic media (HCl, $CHCl_3$, 25 °C, 24 h). Under mildly basic conditions (0.4 M Et_3N, CH_2Cl_2, 25 °C), **3a** (R = Et) reached equilibrium with **4a** (R = Et) over an 18-h period (**3a**:**4a** = 3:2); however, with weaker bases, such as pyridine (CD_3OD, 25 °C), neither epimerization nor H–D exchange was noted after 3 days.[8] One plausible explanation for the low kinetic acidity observed in these systems could be associated with A(1,3) strain conformational effects.[12] As can be seen from the X-ray structure of **3a** (R = Et) (view B, Figure 1), the acyclic methine hydrogen (H_α) is predisposed to lie nearly orthogonal to the π-system of the adjacent imide carbonyl function due to the minimization of nonbonding interactions between chiral auxiliary, methyl, and propionyl substituents. Accordingly, those transition states wherein *both* carbonyl functions are stereoelectronically disposed to contribute to H_α acidification will be *destabilized* by developing A(1,3) interactions

(4) A typical cannulation time of ca. 30 s was employed.
(5) The desired products were isolated by dilution of the quenched reaction with water followed by methylene chloride extraction. The organic extract was washed successively with aqueous $NaHCO_3$, and brine, then dried (Na_2SO_4), and concentrated in vacuo.
(6) The general descriptor X_C will be employed for either the valine (X_V) or norephedrine (X_N) chiral auxiliaries.
(7) Chromatographic resolution was readily carried out under pressure by using prepacked Merck LoBar silica gel 60 columns.
(8) Diastereomer analyses of **3** and **4** were carried out by HPLC (Waters Radial-Pak B silica gel columns).
(9) Satisfactory elemental analyses and spectral data were obtained for all compounds reported herein.
(10) Parikh, J. R.; von E. Doering, W. *J. Am. Chem. Soc.* **1967**, *89*, 5505.
(11) To a 0.1 M solution of alcohol in 1:1 CH_2Cl_2–Me_2SO at 0 °C were added 3 equiv of Et_3N and 3 equiv of SO_3·py complex. After a reaction time of 30 min, the products were isolated according to the procedures cited in ref 10. Anhydrous reagents and solvents should be employed.
(12) (a) Johnson, F. *Chem. Rev.* **1968**, *68*, 375. (b) Johnson, F.; Malhotra, S. K. *J. Am. Chem. Soc.* **1965**, *87*, 5492, 5493.

Scheme II



between either propionyl or methyl substituents and the imide nitrogen substituents associated with the chiral auxiliary.[13] Stated in an alternative manner, the above-mentioned steric effects appear to attenuate the influence of the exocyclic imidic carbonyl toward H_α acidification by the destabilization of that conformation aligning H_α and the carbonyl π-system.

The aforementioned observations relative to the stability of these β-keto imide systems suggests that selective chemical modification of these substrates is feasible. For example, we have found that the highly diastereoselective carbonyl addition reactions illustrated in Scheme II are possible. Reduction of the β-keto imide **3a** (R = Ph) with zinc borohydride (0.02 M substrate in CH_2Cl_2 to which was added 1 molar equiv 0.24 M of $Zn(BH_4)_2$ in ether; 0 °C, 30 min) afforded >100:1 of the β-hydroxy imide **9a** in >95% yield. The analogous reduction of the diastereomeric β-keto imide **4a** (R = Ph) proceeded in quantitative yield with the same level of diastereoselection to afford **10a**. Identical results were obtained in the related reductions of **3a** and **4a** (R = Et), **3b** and **4b** (R = Ph), and **3b** and **4b** (R = Et). In contrast, sodium borohydride was observed to be nonstereoselective with these substrates. These results establish the fact that the proximal, methyl-bearing stereocenter is solely responsible for the observed 1,2-asymmetric induction and that metal ion chelation is a crucial factor in diastereoface selection.[14] More significantly, it has been found that the addition of **3a** and **4a** (R = Ph) (0.2 M in CH_2Cl_2) to a ethereal solution of 3 equiv of methylmagnesium bromide (1.0 M solution in 1:2 Et_2O:CH_2Cl_2, -78 °C, 4 h). cleanly afforded the adducts **9b** and **10b**, respectively, in >90% yield.

In summary, prior to this study, the efficient construction of chiral β-dicarbonyl synthons had not been directly accessible.[15] The direct acylation of these chiral imide enolates now provides a direct entry into this potentially useful class of chiral synthons. More complex applications of this methodology are currently under investigation.

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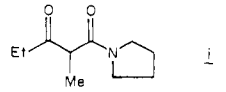
(13) This argument suggests that *N,N*-dialkylamides derived from α-substituted β-keto acids should also exhibit related low kinetic acidities. This is apparent from the one case that we have examined. Amide i exhibited no



i

discernable enol content by ^1H NMR ($CDCl_3$) and no detectable H-D exchange in pyridine-CD_3OD (25 °C, 3 days).

(14) For related reductions, see: (a) Nakata, T.; Oishi, T. *Tetrahedron Lett.* **1980**, *21*, 1641. (b) Nakata, T.; Kuwabara, T.; Tani, Y.; Oishi, T. *Ibid.* **1982**, *23*, 1015. (c) DiPardo, R. M.; Bock, M. G. *Ibid.* **1983**, *24*, 4805.

(15) For an alternative approach to this class of chiral synthons, see: McGarvey, G. J.; Hiner, R. N.; Matsubara, Y.; Oh. T. *Tetrahedron Lett.* **1983**, *24*, 2733.

Functional Fluorocarbon Micelles. Specific Rate Enhancement in the Catalytic Hydrolysis of Phenyl Esters due to Selective Binding of Fluorocarbon and Hydrocarbon Substrates

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Micelles of perfluoroalkyl surfactants have attracted increasing attention in recent years, because of their peculiar physicochemical characteristics compared with those of the hydrocarbon counterparts. Generally speaking, fluorocarbon surfactants give much reduced surface tension[1] and show limited miscibility with hydrocarbon micelles.[2-6] In spite of these peculiarities, their use as functional micelles has, to the best of our knowledge, not been examined.

The present study was initiated on the basis of our presumption that high efficiency and novel selectivity in catalysis are attainable by making use of the peculiar characteristics of fluorocarbon micelles. The catalytic action of cationic hydrocarbon micelles has been extensively investigated especially in the hydrolysis of phenyl esters.[7,8] Therefore, it is interesting to compare the catalytic action by cationic fluorocarbon micelles toward fluorocarbon and hydrocarbon substrates. The structures of catalyst and substrate used in this study and their abbreviations are shown in Chart I.[9]

Zwitterionic long-chain (hydrocarbon) hydroxamates provide efficient, micellar nucleophiles without additional surfactants, and their catalytic behavior in the hydrolysis of hydrocarbon phenyl esters has been examined.[11] We chose the same type of nucleophile in this study. The long-chain moiety is, however, fluorocarbon. The substrates are *p*-nitrophenyl esters, and the acyl portion is either a long-chain fluorocarbon or a hydrocarbon. PNPA is also used as reference.

The catalytic hydrolysis was carried out as follows. A stock solution of the catalyst, which was prepared by sonication (Bransonic Cell Disruptor, 185), was added to a borate buffer solution, and the mixture (3000 μL) was kept at 30 °C in a UV cell. The reaction was initiated by adding 10 μL of substrate in acetonirile (< 0.5 vol % of the reaction mixture), and the rate of hydrolysis was estimated by appearance of *p*-nitrophenolate (400 nm). The catalyst was always used in excess, and the pseudo-first-order rate law was satisfied up to at least 80% of reaction. The spontaneous rate (alkaline hydrolysis) was negligibly small. The extent of dissociation of the hydroxamic acid unit (α) was determined by UV titration of the hydroxamate anion (240 nm).[11,12]

Figure 1 describes the dependence of the pseudo-first-order rate constant for the hydroxamate anion, k_1 ($=k_{obsd}/\alpha$), on the catalyst concentration. Because of the large rate difference, a low medium pH (6.3) was selected for the combination of C^F_{10}-HA-C_4N^+ and C^F_{10}-PNP, and a higher pH (7.6) was used for the other systems. The C^F_{10}-PNP substrate hydrolyzed with remarkable efficiency, and the rate saturation is complete in the presence of ca. 20 equiv

(1) Schwartz, E. G.; Reid, W. G. *Ind. Eng. Chem.* **1964**, *56*, 26-31.
(2) Mukerjee, P.; Yang, A. Y. S. *J. Phys. Chem.* **1976**, *80*, 1388-1390.
(3) Mysels, K. J. *J. Colloid Interface Sci.* **1978**, *66*, 331-334.
(4) Mukerjee, P.; Mysels, K. J. *ACS Symp. Ser.* **1975**, *No. 9*, 239-252.
(5) Funasaki, N.; Hada, S. *Chem. Lett.* **1979**, 717-718; *J. Phys. Chem.* **1980**, *84*, 736-744.
(6) Shinoda, K.; Nomura, T. *J. Phys. Chem.* **1980**, *84*, 365-369.
(7) Fender, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.
(8) Kunitake, T.; Shinkai, S. *Adv. Phys. Org. Chem.* **1981**, *17*, 435-487.
(9) The preparations of C^F_{10}-HA-C_4N^+ (waxy solid) and C^F_{10}-PNP (mp 69.5-70.5 °C) were described briefly elsewhere.[10]
(10) Ihara, H.; Hashiguchi, Y.; Kunitake, T. *Chem. Lett.* **1983**, 733-736.
(11) Kunitake, T.; Okahata, Y.; Tanamachi, S.; Ando, R. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1967-1971.
(12) Katchalsky, A.; Shavit, N.; Eisenberg, H. *J. Polym. Sci.* **1954**, *13*, 69-84.

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