4-methyl acetanilide (9) (25.5% yield), mp 167-169 °C (CH_2Cl_2/petroleum ether) (lit.[13] mp 169-170 °C).

At Room Temperature. Repetition of the previous reaction at ca. 22 °C gave rise to a complex mixture, which was purified by PTLC (SiO_2; CH_2Cl_2), yielding 4,4'-dimethylazobenzene (11) [10% yield; mp 142-144 °C (MeOH) (lit.[14] mp 143 °C], 4,4'-dimethylazoxybenzene (12) [15% yield; mp 67-69 °C (MeOH) (lit.[15] mp 68 °C)], 4-methylacetanilide (10) [11% yield; mp 146-148 °C (CH_2Cl_2/petroleum ether) (lit.[16] mp 146-146.5 °C; IR (KBr) 3280 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (s, 3 H)], 2-hydroxy-4-methylacetanilide (9) [34% yield; mp 168-169 °C (CH_2Cl_2/petroleum ether) (lit.[13] mp 169-170 °C); IR (KBr) 3260, 3100, and 1640 cm^{-1}, ^{1} H NMR ($CDCl_3$) δ 2.26 (s, 3 H)], and *N*-acetyl-*N*-(4-methylphenyl)hydroxylamine (**6b**) [5% yield; mp 71-73 °C (CH_2Cl_2/petroleum ether)] identical with an authentic sample.

Reaction between 5a,f and 4-Nitrobenzoyl Chloride. To a solution of **1a** (0.1 M) in dry benzene at room temperature was added **2** (1 equiv) and the reaction monitored by TLC (SiO_2; CH_2Cl_2) until completion (ca. 2 h). TLC showed the mixture to contain essentially **5a** [IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H)], contaminated with a small amount (≤15%) of **6a**, which was removed by shaking the organic phase with a cold (0-5 °C) aqueous solution of NaOH, 1 N, until the organic phase no longer gave a positive test with ferric chloride (absence of hydroxamic acid). To the benzene solution, after washing with water, drying with anhydrous Na_2SO_4, and filtering, were added solid sodium bicarbonate (1 equiv) and 4-nitrobenzoyl chloride (1 equiv) dissolved in dry benzene. The reaction was left to react at room temperature for 24 h, and after filtration, evaporation of the solvent, and crystallization of the residue from dichloromethane/petroleum ether, **7a** was obtained (18.5% yield): mp 146.5-148 °C; IR (KBr) 1780 and 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (s, 3 H), 7.33 (s, 5 H), 7.68 (d, J = 9 Hz, 2 H), 8.13 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33. Found: C, 60.29; H, 4.08; N, 9.35.

Similarly, **7f** was obtained (29% yield): mp 162-163 °C (dichloromethane/petroleum ether); IR (KBr) 1770 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3 H), 7.22 (d, J = 7.5 Hz, 2 H), 7.48 (d, J = 7.5 Hz, 2 H), 7.70 (d, J = 8.7 Hz, 2H), 8.18 (d, J = 8.7 Hz, 2 H). Anal. Calcd for $C_{15}H_{11}BrN_2O_5$: C, 47.52; H, 2.92; N, 7.39. Found: C, 47.58; H, 3.15; N, 7.52.

General Method for the Preparation of Hydroxamic Acids. To a cooled (0-5 °C) solution of *N*-arylhydroxylamine (ca. 0.2 M) in dry benzene or diethyl ether containing in suspension sodium bicarbonate (1.1 equiv) was added acyl chloride (1.1 equiv). The reaction was monitored by TLC (SiO_2; CH_2Cl_2/MeOH, 100:1; red color upon spray with an aqueous solution of ferric chloride). The hydroxamic acid was isolated after filtration of the reaction mixture, evaporation of the solvent, and crystallization of the residue.

***N*-Acetyl-*N*-phenylhydroxylamine (6a)**: 86% yield; mp 64-66 °C (ethyl acetate/petroleum ether) (lit.[17] mp 65-66 °C); IR (KBr) 3020 and 1630 cm^{-1}; ^1H NMR (CD_3CN) δ 2.18 (s, 3 H), 7.27-7.60 (m, 5 H), 8.42 (br s, 1 H, OH).

***N*-Acetyl-*N*-(4-methylphenyl)hydroxylamine (6b)**: 80% yield; mp 71-72.5 °C (dichloromethane/petroleum ether) (lit.[18] mp 72-73 °C); IR (KBr) 3120 and 1625 cm^{-1}; ^1H NMR (CD_3CN) δ 2.14 (s, 3 H), 2.27 (s, 3 H), 7.19 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H).

***N*-Acetyl-*N*-(4-bromophenyl)hydroxylamine (6f)**: 80% yield; mp 129-130 °C (dichloromethane/petroleum ether) (lit.[19] mp 130-132 °C); IR (KBr) 3140 and 1615 cm^{-1}; ^1H NMR (CD_3CN) δ 2.09 (s, 3 H), 7.71 (d, J = 9 Hz, 2 H), 8.18 (d, J = 9 Hz, 2 H), 8.54 (br s, 1 H, OH).

***N*-(4-Nitrobenzoyl)-*N*-phenylhydroxylamine (8a)**: 66% yield; mp 157-159 °C (dichloromethane/petroleum ether) (lit.[20] mp 163 °C); IR (KBr) 3170 and 1610 cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 7.25 (t, J = 7.5 Hz, 1 H), 7.42 (t, J = 7.5 Hz, 2 H), 7.67 (d, J = 8.7 Hz, 2 H), 7.92 (d, J = 8.7 Hz, 2 H), 8.29 (d, J = 7.5 Hz, 2 H).

***N*-(4-Nitrobenzoyl)-*N*-(4-bromophenyl)hydroxylamine (8f)**: 73% yield; mp 140-141.5 °C (dichloromethane/petroleum ether); IR (KBr) 3100 and 1590 cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 7.59 (d, J = 8.7 Hz, 2 H), 7.70 (d, J = 7.5 Hz, 2 H), 7.95 (d, J = 7.5 Hz, 2 H), 8.31 (d, J = 8.7 Hz, 2 H), 10.08 (br s, 1 H, OH). Anal. Calcd for $C_{13}H_9BrN_2O_4$: C, 46.31; H, 2.69; N, 8.31. Found: C, 46.15; H, 2.81; N, 8.24.

Acetylation of 8a and 8f. To a solution at room temperature of the hydroxamic acid (0.25 M) in dry benzene containing sodium bicarbonate (1.1 equiv) was added acetyl chloride (1.1 equiv). The reaction mixture after standing for ca. 24 h (until no more hydroxamic acid was detected by TLC) was filtered, the solvent distilled under reduced pressure, and the residue crystallized from dichloromethane/petroleum ether. *O*-Acetyl-*N*-(4-nitrobenzoyl)-*N*-phenylhydroxylamine (**7a**) and *O*-acetyl-*N*-(4-nitrobenzoyl)-*N*-(4-bromophenyl)hydroxylamine (**7f**) were obtained with melting points, mixed melting points, and spectroscopic properties identical with those of compounds isolated from the reaction between **5a** or **5f** and 4-nitrobenzoyl chloride.

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Registry No. **1a**, 100-65-2; **1b**, 623-10-9; **2**, 631-57-2; **1f**, 10468-46-9; **6a**, 1795-83-1; **6b**, 27451-21-4; **6f**, 67274-48-0; **7a**, 19958-60-2; **7f**, 108009-19-4; **8a**, 2029-61-0; **8f**, 108009-20-7; **9**, 13429-10-2; **10**, 103-89-9; **11**, 501-60-0; **12**, 955-98-6.

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One-Pot Preparation of Tertiary Alkyl Carboxylates and Sulfonates from Ketones

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Carboxylic and sulfonic acid esters are important categories of organic compounds useful in both synthetic applications and mechanistic studies. The commonly employed preparation method is the reaction of alcohols and acid chlorides in basic media.[1,2] For reactive tertiary alkyl esters the use of the corresponding metal alcoholates under neutral conditions becomes necessary.[3] Since tertiary alcohols are frequently synthesized by the addition of Grignard reagents to the appropriate carbonyl compounds, the drawbacks of such reactions, e.g., steric hindrance to additions, intolerance of labile groups, and the possibility of elimination in isolation steps, make the two-step preparation inconvenient. An improved method, using organolithium reagents followed by esterification, has been used for preparing highly hindered tertiary *p*-nitrobenzoates.[4]

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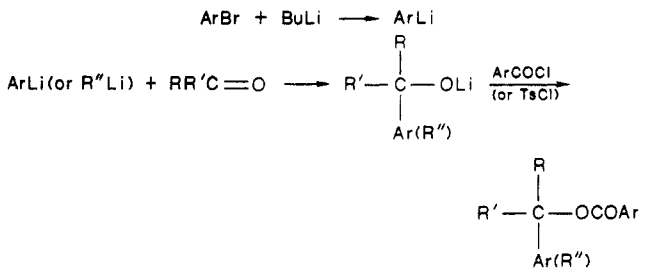
Table I. Preparation of Esters from Ketones

entry	ketone (RR'C=O)	ArLi or R''Li	acid chloride[a]	product[b] mp, °C	product[b] yield, %[c]
1	R = R' = Ph	Ar = 4'-$CF_3C_6H_4$	PNBCl	145–145.5	53
2	R = R' = Ph	Ar = Ph	BzCl	173–174	81
3	R = Ph, R' = CF_3	Ar = 4'CNC_6H_4	TsCl	88–88.5	65
4	R = Ph, R' = CF_3	Ar = Ph	PNBCl	137.5–138	60
5	R = R' = *t*-Bu	Ar = 4'-$CF_3C_6H_4$	PNBCl	188–189 (lit.[d] 192–193)	59
6	R = CH_3, R' = *t*-Bu	Ar = Ph	PNBCl	105–106 (lit.[e] 95–96)	46
7	R = CH_3, R' = *t*-Bu	Ar = 3'-$CF_3C_6H_4$	PNBCl	150–151	52
8	cyclopentanone	Ar = 3'-$CF_3C_6H_4$	PNBCl	107.5–108	56
9	adamantanone	R'' = *i*-Pr	PNBCl	159.5–160 (lit.[f] 158.5–159)	50

[a] PNBCl, *p*-nitrobenzoyl chloride; BzCl, benzoyl chloride; TsCl, *p*-toluenesulfonyl chloride. [b] All new compounds gave satisfactory analytical (C, H or C, H, N) and spectral (^{1}H NMR and IR) data for the assigned structure. [c] Isolated yields of purified products (recrystallization) from 6 mmol of ketones. [d] Reference 4. [e] Reference 8. Although the mp is quite different, our sample gave correct spectral data in line with the assigned structure. [f] Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628–4634.

Scheme I



While the complex mixture produced could be purified by tedious separation on thin-layer chromatography,[4] the method was inapplicable to reactive esters, such as 1,1-diphenylethyl *p*-nitrobenzoate.[5] We wish to report a convenient one-pot preparation to circumvent the above-mentioned shortcomings.

Reduction, condensation, or enolization of carbonyl substrates[6] and substitution of haloalkanes produced in halogen–metal exchange reactions[7] are all known to occur with organolithium compounds in different circumstances, although all can be minimized at lower temperature. In a preliminary study we found that at −100 °C the metal–halogen exchange between butyllithium and aryl halide and the addition of the resulting aryllithium to ketones were complete in an hour without intervention of substitution or other side reactions. Moreover, the reaction of organolithium compounds with nitriles could be avoided under this condition.[7] On the basis of these facts we undertook development of a convenient procedure for preparing tertiary carboxylic and sulfonic acid esters.

Aryl bromides in THF–hexane (4:1) were allowed to react with butyllithium at −100 °C to generate aryllithium in situ. To this or to other alkyllithiums was added a THF solution of ketone to form a tertiary lithium alcoholate, which was then, without isolation, esterified with an appropriate acyl chloride or sulfonyl chloride to give the desired carboxylate ester in 1–5 h or the sulfonate ester in 24–48 h (Scheme I). Isolated yields of pure esters ranged from 46% to 81% as shown in Table I.

This one-pot procedure has several advantages. First, it is versatile and simple; second, the overall yields are in general considerably higher than those obtained either in a two-step process, e.g., 46% in entry 6 vs. 23% from the conventional method (Grignard addition of *tert*-butylmagnesium bromide to acetophenone followed by the reaction of the resulted alcohol with *p*-nitrobenzoyl chloride),[8] or in the preparation under uncontrolled conditions, e.g., 59% in entry 5 vs. 39%.[4] A variety of ketones, from the unhindered cyclopentanone (entry 8) to the highly crowded 2,2,4,4-tetramethyl-3-pentanone (entry 5), have been employed. No correlation of yields with the steric hindrance of ketones or with the stability of esters was observed.

The high yield of triphenylmethyl benzoate (entry 2) suggests the importance of the molecular symmetry to yield. The compatibility of nitriles with this procedure could be demonstrated by the good yield (65%) of 1-(4-cyanophenyl)-1-phenyl-2,2,2-(trifluoroethyl) tosylate (entry 3).

Experimental Section

Capillary melting points were uncorrected. IR spectra (KBr) were recorded with a Perkin-Elmer Model 983G spectrometer and ^{1}H NMR with a Varian Model EM390 instrument. Elemental analyses were performed here in the Elemental Analysis Laboratory.

Preparation of 2,2,2-Trifluoro-1,1-diphenylethyl *p*-Nitrobenzoate. General Procedure. A 100-mL round-bottomed flask with a serum-capped side arm, stirring bar, condenser with drying tube, and nitrogen inlet tube, was hot blower-dried under nitrogen. To this was added 6 mmol of bromobenzene in 6 mL of THF–hexane (4:1) through the side arm with a syringe. The solution was chilled to −100 °C, and 6 mmol of butyllithium (1.6 M in hexane) was added dropwise with stirring. It was kept at −100 °C for 10 min, and 6 mmol of α,α,α-trifluoroacetophenone in 5 mL of THF was introduced slowly. The temperature was raised to −78 °C, and after 30 min 6 mmol of *p*-nitrobenzoyl chloride in 5 mL of THF was added slowly. After 10 min at −78 °C, the temperature was allowed to rise to room temperature (1 h). The esterification was monitored by TLC and stirring continued for an additional 1–2 h, as necessary. The solvent was stripped off, and 10 mL of diethyl ether was added. The ethereal solution obtained after filtration was washed successively with ice-chilled 5% sodium bicarbonate and then ice–water. It was dried ($MgSO_4$) and evaporated to dryness in vacuo. The crude ester was recrystallized from hexane to give pure compound: mp 137.5–138 °C (60% yield); IR (KBr) 1744 (s) (C=O), 1518 (s) and 1350 (s) (NO_2), 1270 cm^{-1} (s) (C–O); ^{1}H NMR (CCl_4) δ 8.28 (4 H, C_6H_4), 7.23 (10 H, m, C_6H_5). Anal. ($C_{21}H_{14}NO_4F_3$) C, H, N.

Other *p*-nitrobenzoates were prepared in the same way with the exception of 2-isopropyl-2-adamantyl *p*-nitrobenzoate, for which the isopropyllithium solution (prepared from lithium and 2-chloropropane) was added to adamantanone directly (entry 9).

Preparation of Triphenylmethyl Benzoate. The above-mentioned general procedure was followed, but a longer reaction time (5 h) was required for esterification. The benzoate ester was obtained in 81% yield: mp 173–174 °C; IR (KBr) 1721 (s) (C=O), 1273 cm^{-1} (s) (C–O); ^{1}H NMR (CCl_4) δ 8.05 (2 H, dd), 7.30 (18 H, m). Anal. ($C_{26}H_{20}O_2$) C, H.

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Preparation of 1-(4-Cyanophenyl)-1-phenyl-2,2,2-trifluoroethyl Tosylate. The titled compound was synthesized from butyllithium, 4-bromobenzonitrile, α,α,α-trifluoroacetophenone, and tosyl chloride following the general procedure for the preparation of *p*-nitrobenzoates. Esterification at room temperature for 24 h followed by separation and recrystallization gave 65% yield of the tosylate: mp 88–88.5 °C; IR (KBr) 2232 (m) (CN), 1376 (s) and 1171 (s) (O_3SAr), 1194 cm^{-1} (s) (CF_3); ^1H NMR (CCl_4) δ 2.42 (3 H, s, CH_3), 7.30 (8 H, m), 7.59 (5 H, s, C_6H_5). Anal. ($C_{22}H_{16}NO_3F_3S$) C, H, N.

Acknowledgment. We are indebted to the National Science Council for financial support of this work.

Registry No. PNBCl, 122-04-3; $PhC(O)CF_3$, 434-45-7; *t*-Bu_2CO, 815-24-7; *t*-$BuC(O)CH_3$, 75-97-8; 4-$CF_3C_6H_4Br$, 402-43-7; PhBr, 108-86-1; 4-CNC_6H_4Br, 623-00-7; 3-$CF_3C_6H_4Br$, 401-78-5; *i*-PrCl, 75-29-6; Ph_2CO, 119-61-9; BzCl, 98-88-4; TsCl, 98-59-9; $Ph_2C(4\text{-}CF_3C_6H_4)OC(O)\text{-}4\text{-}C_6H_4NO_2$, 108418-82-2; $Ph_3COC(O)Ph$, 17714-77-1; $PhC(CF_3)(4\text{-}CNC_6H_4)OSO_2\text{-}4\text{-}C_6H_4Me$, 108418-83-3; $Ph_2C(CF_3)OC(O)\text{-}4\text{-}C_6H_4jNO_2$, 108418-84-4; *t*-$Bu_2C(4\text{-}CF_3C_6H_4)OC(O)\text{-}4\text{-}C_6H_4NO_2$, 40544-07-8; $CH_3C(t\text{-}Bu)(Ph)OC(O)\text{-}4\text{-}C_6H_4NO_2$, 42044-42-8; $CH_3C(t\text{-}Bu)(3\text{-}CF_3C_6H_4OC(O)\text{-}4\text{-}C_6H_4NO_2$, 108418-85-5; cyclopentanone, 120-92-3; adamantanone, 700-58-3; 1-[[(4-nitrophenyl)carbonyl]oxy]-1-[3-(trifluoromethyl)phenyl]cyclopentane, 108418-86-6; 2-[[(4-nitrophenyl)carbonyl]oxy]-2-isopropyladamantane, 38432-73-4.

Preparation of Enaminones by Two-Carbon Homologation of Amides with Lithium (Triphenylsilyl)acetylide

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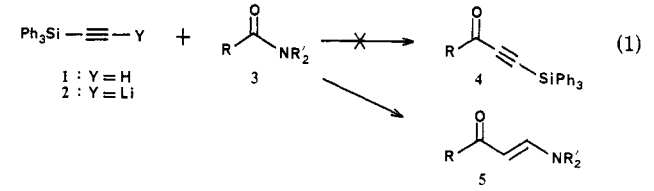
Enaminones[1] constitute a class of compounds that are versatile for the synthesis of heterocyclic or aromatic compounds.[2] They are used in some other useful synthetic transformations.[3] Therefore, a variety of their preparative methods have been reported thus far.[4]

During the course of our recent investigations,[5] we encountered an unexpected formation of enaminones during the reaction of lithium (triphenylsilyl)acetylide (**2**) with carboxamides (eq 1): attempted reaction of **2** with amide



(1)

3 gave none of the expected alkynone **4**, although the starting material was completely consumed. TLC inspection indicated the formation of a highly polar product which was isolated and identified as the two-carbon-inserted enaminone **5**. This outcome can be understood by the following sequence of events: the initial formation of the silylalkynone followed by the Michael-type addition of in situ-formed lithium amide and subsequent protiodesilylation.[6] A D_2O-quenching experiment showed the double incorporation of deuterium into the product (Figure 1), where D^α underwent gradual replacement by a proton under certain conditions such as the purification on silica gel TLC. Intrigued by these observations and also considering the synthetic utility of enaminones, we briefly surveyed the scope of the present unexpected reaction.

Table I represents some aspects of the reaction. While amides with a Me_2N or pyrrolidino group were smoothly converted to the enaminones **5** (entries 1, 2, 4, 5), the amides bearing bulkier amino groups such as Et_2N (entry 3) or Ph_2N (not shown) gave none of the corresponding enaminones. Concerning the substituents on silicon, *triphenyl* is essential for smooth enaminone formation, and other silylacetylides (e.g. *t*-$BuMe_2SiC{\equiv}CLi$) gave the normal product **4**.[7,8]

Aside from these features, application to the two-carbon ring expansion of cyclic amides (entries 6–8) is notable: five to seven-membered *N*-methyl lactams underwent this two-carbon insertion to afford the corresponding medium-ring azacycles **5f–h**.[9] In these cases, a slight modification of the reaction conditions (method B; see Experimental section) was necessary, that is, (1) the use of $BF_3{\cdot}OEt_2$,[10] which is essential for the addition reaction to proceed, and (2) the use of a less polar solvent mixture (hexane–THF, 5/1) for the improvement of the yields.[11]

Experimental Section

General. Infrared (IR) spectra were recorded on a JASCO A-202 spectrometer. ^1H NMR spectra were measured on a Varian EM 390 spectrometer at 90 MHz. ^{13}C NMR spectra were measured on a JEOL GX 400 spectrometer at 100 MHz. The chemical shifts are expressed in parts per million downfield from internal tetramethylsilane (δ = 0). Mass spectra (MS) were obtained with a Hitachi M-80 spectrometer. All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis, Merck precoated plates (silica gel 60 GF 254, 0.25 mm) were used. The products were purified by preparative TLC

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(5) Suzuki, K.; Ohkuma, T.; Miyazawa, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1986**, *27*, 373.

(6) Reaction of $MeCOC{\equiv}CSiPh_3$ (prepared by the Friedel–Crafts reaction, i.e., $AcCl—Ph_3SiC{\equiv}CSiPh_3—AlCl_3$: Newman, H. *J. Org. Chem.* **1973**, *38*, 2254) with lithium salt of pyrrolidine in THF gave almost quantitative yield of the corresponding enaminone **5**.

(7) Reaction of Me_3Si- or *t*-$BuMe_2Si$-acetylide gave the corresponding alkynone **4**, while Ph_2MeSi-acetylide gave a varying mixture of **4** and **5** depending on the conditions. For the related examples of Me_3Si cases, see: Cupps, T. L.; Boutin, R. H.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 3972.

(8) Since the Michael addition of amines to alkynones is known,[4c,d] the transformation (**3**→**5**) is formally possible simply by using $LiC{\equiv}CH$. However, this protocol appeared to be inefficient in this context, where the use of excess reagents or forcing conditions led to the complex mixture of products.

(9) For related ring expansion of lactones, see: Schreiber, S. L.; Kelly, S. E. *Tetrahedron Lett.* **1984**, *25*, 1757.

(10) Yamaguchi, M.; Waseda, T.; Hirao, I. *Chem. Lett.* **1983**, 35.

(11) The reaction using $BF_3{\cdot}OEt_2$ should be stopped with aqueous acids, such as CH_3COOH, $(COOH)_2$, etc. Substantial decomposition of the products occurred with MeOH or H_2O quenching.

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