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PPh_3-Catalyzed Reactions of Alkyl Propiolates with *N*-Tosylimines: A Facile Synthesis of Alkyl 2-[aryl(tosylimino)methyl]acrylate and an Insight into the Reaction Mechanism

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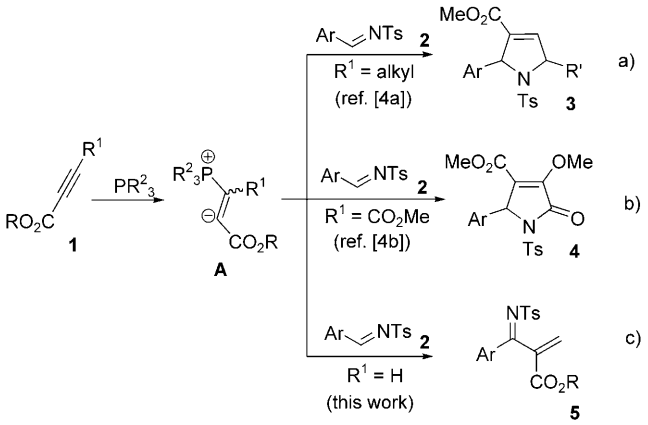
Abstract: A new PPh_3-catalyzed synthesis of alkyl 2-[aryl(tosylimino)methyl]acrylates from propiolate and *N*-tosylimine has been developed. Deuterium-labelling experiments show that the reaction mechanism involves several hydrogen-transfer processes, which are not the turnover-limiting step and strongly rely on the nature of the reaction media. The stable phosphonium–enamine zwitterion, which was proven to play an important role in the catalytic cycle, has been isolated and characterised by X-ray analysis.

Keywords: hydrogen transfer · imines · phosphanes · reaction mechanisms · zwitterions

Introduction

Much development in the chemistry of tertiary phosphanes as nucleophilic catalysts has been achieved in the past few decades.[1] This success might be ascribed to the properties of tertiary phosphanes, such as strong nucleophilicity and ease of ylide formation, as well as leaving group ability. The combination of these unique properties allows tertiary phosphanes to perform 1,4-conjugate additions to α,β-unsaturated carbonyl compounds, to stabilise an adjacent carbanion and to serve as an efficient leaving group. Furthermore, the readily available variants of α,β-unsaturated carbonyl compounds also provides this field with a large number of possibilities for discovering new phosphane-catalyzed reactions.

In the case of the phosphane-catalyzed reactions of activated alkynes **1** with *N*-tosylimines **2**, 1,3-zwitterions **A** are generally postulated to be versatile intermediates.[2] Reactivity strongly relies on the substituent R^1 at the β position of alkyne **1** (Scheme 1).[3] When R^1 is an alkyl group, a [3+2] cycloaddition reaction occurs to yield **3** (Scheme 1a).[4a] Alternatively, the reaction pathway will be switched to produce compound **4** if the R^1 group is a carboxylate (Scheme 1b).[4b] However, to the best of our knowledge, there has been no success reported in the PR_3-catalyzed reactions of alkyl propiolates (R^1=H) with *N*-tosylimines.[5] Propiolates have attracted increasing attention in the chemistry of C3-homologation agents due to their versatile reactivity profile.[6] Herein, we report a new PPh_3-catalyzed reaction of propiolate with *N*-tosylimine to give alkyl 2-[aryl(tosylimino)methyl]acrylate (**5**) under simple conditions (Scheme 1c). We also comprehensively investigated the reaction mechanism and some significant details are disclosed.



Scheme 1. Reactivity of intermediate **A** as the nucleophile.

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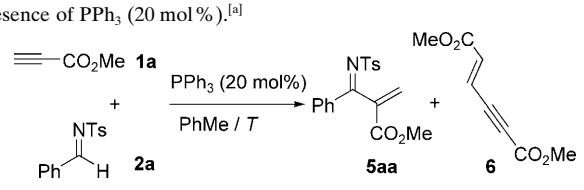
Results and Discussion

When a mixture of methyl propiolate (**1a**) and phenyl tosylimine (**2a**) was treated with a catalytic amount of PPh_3 (20 mol%) in toluene at room temperature for 24 h, the corresponding product **5aa** was obtained in only 6% yield (Table 1, entry 1). At elevated temperatures, there was no

Table 1. Optimised conditions for the reaction between **1a** and **2a** in the presence of PPh_3 (20 mol%).[a]



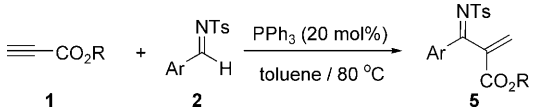
Entry	**1a** [equiv]/[M][b]	Method	*T* [°C]	*t* [h]	Yield [%][c] **5aa**	**6**
1	3.0/0.6	A	25	24	6	20
2	3.0/0.6	A	50	12	8	32
3	3.0/0.6	A	80	12	18	40
4	3.0/0.6	A	120	12	ND[d]	
5	3.0/0.4	B	80	3	28	0
6	2.0/0.3	B	80	3	31	0
7	1.2/0.24	B	80	3	46	0
8	1.2/0.06	B	80	3	51	0
9	1.2/0.03	B	80	3	13	0

[a] Reaction conditions: method A: **1a**, **2a** (1.0 mmol) and PPh_3 (0.2 mmol) in toluene (5 mL) were mixed before the reaction was conducted at the temperature indicated under N_2; method B: the solution of **1a** in toluene was slowly added to a mixture of **2a** (1.0 mmol) and PPh_3 (0.2 mmol) in toluene (10 mL) at 80 °C under N_2 within 3 h. [b] [M]: concentration of **1a** in toluene (mol L^{-1}). [c] Yield of the isolated product. [d] ND = no product detected.

obvious improvement in the yield of **5aa** (Table 1, entries 2–4). However, compound **6**, the dimer of **1a**,[7] was obtained in up to 40% yield in these cases (Table 1, entries 1–3). To avoid the consumption of **1a** through dimerisation, the solution of **1a** in toluene was slowly added into the reaction mixture of **2a** and PPh_3 over 3 h to maintain a low concentration of **1a** (Table 1, entry 5). Hence, the yield was increased to 28%. A concentration of 0.06 mol L^{-1} of **1a** was found to be optimum, with which **5aa** could be obtained in 51% yield (Table 1, entry 8). The solvent was so crucial for this transformation that other solvents, such as THF, benzene, hexane, dioxane, DMSO, CH_2Cl_2 and CH_3CN, led to non-selective reactions with complete consumption of **2a**.

With the optimised conditions in hand (Table 1, entry 8), we directed our subsequent efforts towards testing the scope of this reaction (Table 2). Besides **1a**, (Table 2, entries 1–6), both benzyl propiolate (**1b**) (Table 2, entries 7 and 8) and 2-ethoxy-2-oxoethyl propiolate (**1c**) (Table 2, entry 9) can be employed as substrates and deliver similar results. However, other partners, namely, *N*-tosylimines **2a–g**, impose more significant electronic effects on this transformation. Higher yields can be obtained when *N*-tosylimines **2** possess electron-donating groups on the phenyl ring (Table 2, entries 2 and 8), whereas *N*-tosylimines **2** with electron-deficient

Table 2. Reactions of **1** with **2** in the presence of PPh_3 (20 mol%).[a]

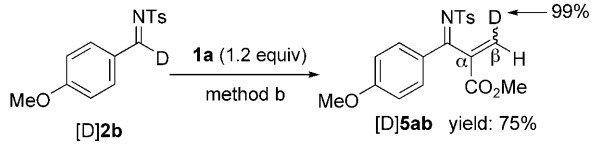


Entry	R (**1**)	Ar (**2**)	Yield [%][b]
1[c]	Me (**1a**)	Ph (**2a**)	50 (**5aa**)
2[c]	Me (**1a**)	4-MeO-C_6H_4 (**2b**)	89 (**5ab**)
3	Me (**1a**)	4-Me-C_6H_4 (**2c**)	77 (**5ac**)
4	Me (**1a**)	4-Br-C_6H_4 (**2d**)	46 (**5ad**)
5	Me (**1a**)	4-Cl-C_6H_4 (**2e**)	40 (**5ae**)
6	Me (**1a**)	piperonyl (**2f**)	66 (**5af**)
7	Bn (**1b**)	Ph (**2a**)	55 (**5ba**)
8	Bn (**1b**)	4-MeO-C_6H_4 (**2b**)	80 (**5bb**)
9	CH_2CO_2Et (**1c**)	4-MeO-C_6H_4 (**2b**)	62 (**5cb**)
10	Me (**1a**)	4-NO_2-C_6H_4 (**2g**)	0 (**5ag**)

[a] Reaction conditions: method B. For details see the Supporting Information. [b] Yield of the isolated product. [c] The reaction was carried out on a scale of **1a** (7.2 mmol) and **2** (6 mmol) in toluene (60 mL).

groups on the phenyl ring resulted in lower yields (Table 2, entries 4 and 5). Especially, in the case of substrate **2g**, which has an NO_2 group on the phenyl ring, no desired product of **5ag** was obtained (Table 2, entry 10) and (*E*)-methyl 3-tosylacrylatein (**7**) was isolated in 6% yield instead.

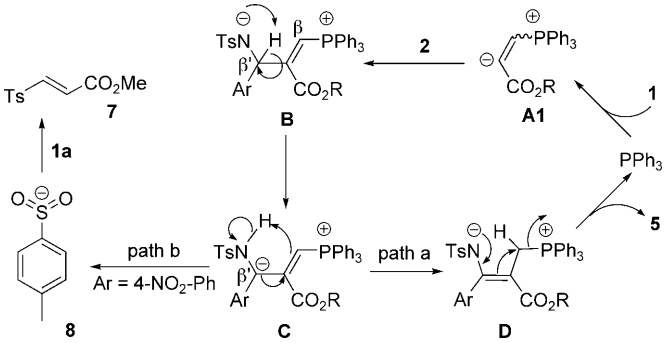
To better understand the mechanism of this transformation, we conducted the reaction with the deuterium-labelled substrate [D]**2b** (Scheme 2). The deuterium atom was com-



Scheme 2. Reaction with deuterium-labelled substrate.

pletely incorporated into product [D]**5ab** at the β carbon atom and was located in either the *cis* or *trans* position with a ratio of 1:1 (see the Supporting Information for details).

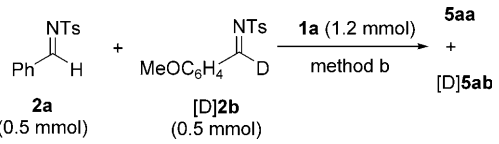
On the basis of the results shown in Table 2 and Scheme 2, a reaction mechanism is outlined in Scheme 3.



Scheme 3. Proposed mechanism.

Addition of PPh_3 to **1a** forms the zwitterion **A1**, which undergoes Mannich-type reaction with **2** to give the intermediate **B**. [1,2]-hydrogen transfer converts **B** to the intermediate **C**. Then hydrogen transfer occurs again to provide the intermediate **D**. Finally, [1,5]-elimination of PPh_3 completes the catalytic cycle and gives the product **5**. Based on this proposal, we might elucidate the important role of the aryl group of *N*-tosylimines **2**. The electron-rich aryl groups might contribute significantly to the delocalisation of the β′ carbanion of **C**, which is thought to be a key step in the formation of the intermediate **D** (Scheme 3, path a). On the contrary, the aryl groups with electron-deficient groups might, to some extent, stabilise this carbanion and prevent the formation of the intermediate **D**. When a stronger electron-deficient group, such as NO_2, is introduced, path a (Scheme 3) will be completely shut down and the alternative pathway (path b, Scheme 3) becomes the favourable route to give anion **8**, which will undergo further Michael addition with **1a** to produce compound (*E*)-methyl 3-tosylacrylate (**7**) (Scheme 3).[8]

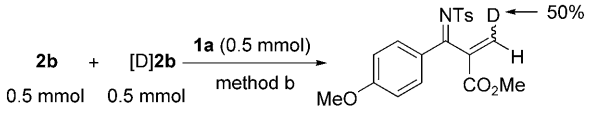
We also carried out a series of control experiments to obtain more mechanistic detail. Firstly, when a 1:1 mixture of **2a** (0.5 mmol) and [D]**2b** (0.5 mmol) was subjected to the reaction conditions in the presence of **1a** (1.2 mmol), no D–H cross products were detected (Scheme 4). This result



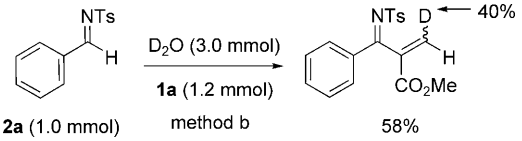
Scheme 4. Control experiment with deuterated and non-deuterated substrates.

strongly indicates that the hydrogen-transfer process occurs intramolecularly. Secondly, when a 1:1:1 mixture of **2b** (0.5 mmol), [D]**2b** and **1a** was employed (Scheme 5), it was found that both **2b** and [D]**2b** reacted at the same rate ($k_H/k_D = 1.0$) (see the Supporting Information). Thus, it can be interpreted that the hydrogen-transfer process is not the turnover-limiting step of the catalytic cycle.[9]

Moreover, the control experiment was also conducted with **1a** and **2a** in the presence of D_2O (3 equiv) (Scheme 6). This reaction was not hindered by the presence of additional D_2O and smoothly proceeded to give product **5aa** in 58% yield.[10] Note that 40% deuterium was incorporated into the product (Scheme 6). These results clearly demonstrate that, in the presence of D_2O, an intermolecular pathway for the hydrogen-transfer process exists, along



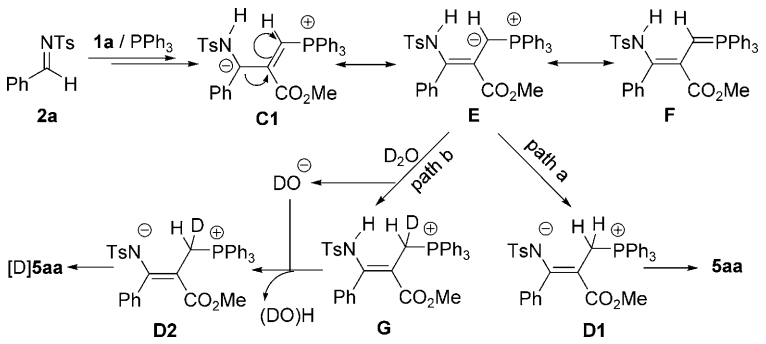
Scheme 5. Control experiment employing a 1:1:1 mixture of **2b**, [D]**2b** and **1a**.



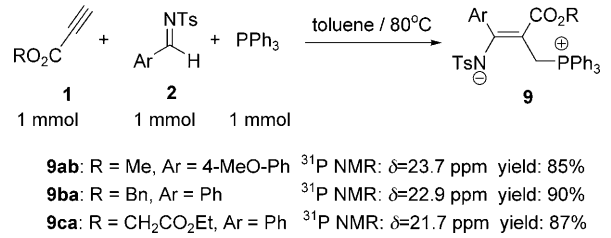
Scheme 6. Control experiment carried out in the presence of D_2O.

with intramolecular pathway.[11] At present, we do not have convincing evidence to clarify the reaction mechanism, but the outcome of the reactions in Schemes 2, 4, 5 and 6 tempts us to discuss it (Scheme 7). Following the same reaction pathway as that in Scheme 3, the interaction between **1a**, **2a** and PPh_3 gives intermediate **C1**. Due to the ability of PPh_3 to stabilise an adjacent carbanion and the ease of formation of the ylide, intermediate **C** may coexist with the other two resonance forms **E** and **F**. In toluene, it is believed that the intramolecular hydrogen-transfer process is fast and **5aa** would be obtained without deuterium incorporation via intermediate **D1** (Scheme 7, path a). We presumed that additional D_2O would change the nature of the polarity of the solvent systems. Therefore, the ion pairs of intermediate **E** might be separated, to some extent, to facilitate the possibility of intermolecular reactions. Therefore, intermolecular hydrogen transfer from D_2O to **E** takes place to release one equivalent of DO^- and produce the deuterium-labelled intermediate **G** (Scheme 7, path b).[12] It is apparent that the deuterium-labelled product [D]**5aa** could ultimately be obtained via intermediates **G** and **D2** (Scheme 7, path b).

To our surprise, only a trace of **5ca** was observed by TLC when the reaction of **1c** and **2a** was carried out in the presence of PPh_3 (1 equiv) (Scheme 8). Fortunately, a dark-coloured solid was obtained after removal of the solvent. This solid could be purified easily by recrystallisation in a mix-



Scheme 7. Different hydrogen-transfer pathways.



9ab: R = Me, Ar = 4-MeO-Ph ^{31}P NMR: δ=23.7 ppm yield: 85%
9ba: R = Bn, Ar = Ph ^{31}P NMR: δ=22.9 ppm yield: 90%
9ca: R = CH_2CO_2Et, Ar = Ph ^{31}P NMR: δ=21.7 ppm yield: 87%

Scheme 8. Formation of the phosphonium–enamine zwitterions; Bn = benzyl.

ture of CH_2Cl_2 and hexane. The structure was determined and assigned as compound **9ca** by spectroscopic data and X-ray diffraction (Figure 1). Two other similar adducts, **9ab** and **9ba**, can also be obtained under identical conditions. Most notably, all of their ^{31}P NMR spectra exhibited a diagnostic signal for tetravalent phosphorus at around $\delta = +22.0$ ppm.[13] Clearly, these phosphorus atoms are identical to that postulated in intermediate **D** in Scheme 3.

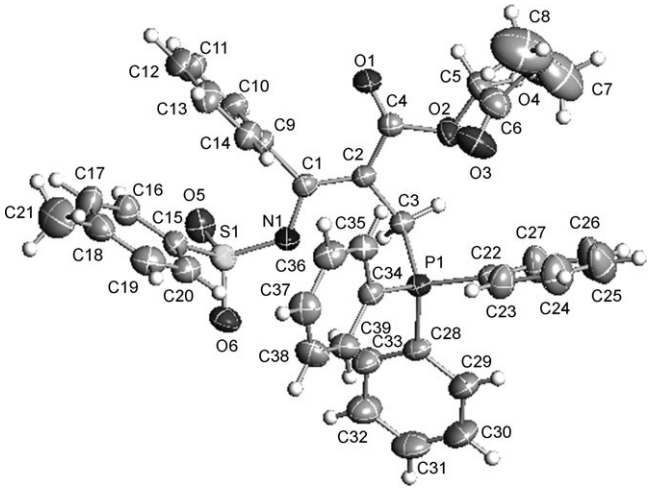
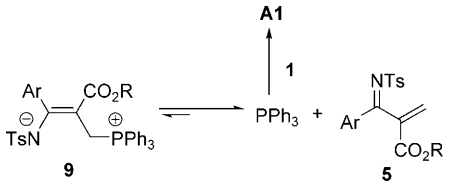


Figure 1. X-ray crystallography of **9ca**. Ellipsoids at 30% probability.

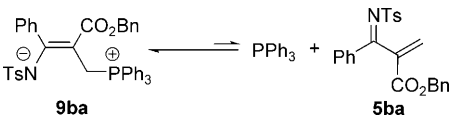
The X-ray crystallographic data for **9ca** (Figure 1) reveals that the phosphorus atom has a tetrahedral geometry and does not bond covalently with the nitrogen atom of the enamine–anion, as evidenced by the P1–N1 distance of 3.355 Å (covalent radii of P and N are 1.05 and 0.68 Å, respectively). Importantly, this structure has long been postulated as one of the key intermediates in aza-Baylis–Hillman reactions.[14] Recently, Kwon et al. reported the first stable phosphonium–enolate zwitterions, which have been unequivocally characterised by using X-ray crystallography.[15] Slightly different from Kwon's elegant work, PPh_3 works well in our research probably because of the introduction of *N*-tosylimine as the electrophile. Therefore, we believe that either electron-releasing alkyl substituents on the phosphonium centre or electron-withdrawing groups on the anion centre play an important role in stabilising the phosphonium zwitterions. These observations might show some common characteristics of phosphane-catalyzed reactions.

Interestingly, the zwitterion **9ba** was quite stable in toluene and did not decompose at all, even at 80 °C.[16] However, when **1a** (1 equiv) was added, zwitterion **9ba** quickly decomposed to yield PPh_3 and **5ba** (Scheme 9). Furthermore,



Scheme 9. Relationship between PPh_3, **1**, **5** and **9**.

when a 1:1 mixture of **5ba** and PPh_3 in toluene was heated at 80 °C for 3 h, the ^{31}P NMR spectrum of the reaction mixture exhibited only one signal, which could be assigned to the zwitterion **9ba** (Scheme 10). On the basis of these results, two important points can be concluded: 1) the zwitterion **9** is qualified to be one intermediate for this catalytic reaction; 2) elimination of PPh_3 from the intermediate **D** is a reversible step, but the balance is mainly shifted towards **D** (Scheme 10). Thus, we assumed that the step in which PPh_3 is eliminated from intermediate **D** would be a likely candidate for the turnover-limiting step of the catalytic cycle. Furthermore, we believe that alkyl propiolates **1** not only work as a reactant, but also as an efficient scavenger of PPh_3 (Scheme 9): the reaction between propiolate and PPh_3 might ensure that the concentration of PPh_3 would be reduced to a very low level, which would destroy the balance of Scheme 10 and facilitate the complete conversion of **9** to **5**. It is also believed to be the reason why intermediate **9** (intermediate **D**) could be isolated when equivalent amounts of PPh_3 and propiolates **1** were used (Scheme 8).



Scheme 10. Balance between **9ba** and **5ba**.

Conclusion

A new PPh_3-catalyzed reaction of alkyl propiolate with *N*-tosylimine to give the adduct alkyl 2-[aryl(tosylimino)methyl]acrylate **5** has been developed. The proposed mechanism involving the hydrogen-transfer process has been established on the basis of a series of deuterium-labelling experiments. It was found that the pathways of the hydrogen-transfer process strongly depend on the nature of the reaction media. Control experiments disclosed that the elimination of PPh_3

from the intermediate **D** can be assigned as the turnover-limiting step of the catalytic cycle. Most importantly, we isolated and characterised some stable phosphonium zwitterions, which were found to be one of the key intermediates in this new reaction. We believe that the highly activated terminal olefin of **5** could be functionalised for further use and the results will be reported in due course.[17] Efforts are also underway to provide more mechanistic details and to extend this study to new PPh_3-catalyzed reactions.

Experimental Section

General procedure for PPh_3-catalyzed reactions: Compound **2a** (1.0 mmol) and PPh_3 (52.4 mg, 20 mmol%) were added to toluene (10 mL) in three-necked flask. The mixture was stirred at 80°C under an N_2 atmosphere. A solution of **1a** (1.2 mmol) in toluene (20 mL) was slowly added to this reaction mixture within 3 h. Once the addition was finished, the reaction mixture was cooled to room temperature. Then the mixture was directly subjected to silica-gel column chromatography to give the product **5aa**. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.91 (d, J=8.4 Hz, 2H), 7.89 (d, J=8.4 Hz, 2H), 7.57 (t, J=7.2 Hz, 1H), 7.43 (t, J=7.6 Hz, 2H), 7.35 (d, J=8. 4 Hz, 2H), 6.85 (s, 1H), 5.94 (s, 1H), 3.80 (s, 3H), 2.46 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=173.6, 163.3, 144.0, 137.5, 137.0, 135.5, 134.0, 130.5, 129.7, 129.5, 128.7, 127.4, 52.4, 21.4 ppm; MS (EI): m/z: 343 [M^+]; HRMS: m/z calcd for $C_{18}H_{17}NO_4S$: 343.3969, found: 343.3971.

Acknowledgements

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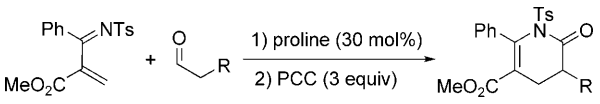
[16] This reaction should be carried out under conditions strictly excluding O_2, otherwise, $Ph_3P(O)$, probably oxidised by the residual O_2, would be detected in the ^{31}P NMR spectrum of the reaction mixture. Meanwhile, compound **5ba** could be also obtained.

[17] The preliminary results of the application of **5** have been demonstrated by the following two-step reaction in a one-pot procedure (PCC=pyridinium chlorochromate):.



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