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Friedel–Crafts Reaction of the Baylis–Hillman Adducts of *N*–Tosylimine Derivatives

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Abstract

Friedel–Crafts reaction of aromatic compounds with the Baylis–Hillman adducts of *N*–tosylimine derivatives in the presence of sulfuric acid provided a stereoselective methodology for the preparation of 2-benzylsubstituted olefins in moderate yields.

Keywords: Friedel–Crafts reaction; Baylis–Hillman adducts; *N*–Tosylimines

In the course of our recent studies on the Friedel–Crafts reaction we have found that certain Lewis basic substrates containing carbon–nitrogen single bond could generate carbocationic species in the presence of sulfuric acid or aluminium chloride [1–2]. Such substrates include 1,3-dicyclohexylcarbodiimide, amides, sulfonamides, and urea derivatives. Based on our results we intended to apply our findings for the preparation of synthetically useful compounds. As a part of our program, we examined on the Friedel–Crafts reaction of sulfonylimine derivatives and their Baylis–Hillman adducts, and herein we wish to describe our preliminary results on the Friedel–Crafts reaction of aromatic compounds with the Baylis–Hillman adducts of *N*–tosylimines.

As shown in Scheme 1 and Table 1, Friedel–Crafts reaction of some arenes with the Baylis–Hillman adducts of *N*–tosylimine derivatives **3** in the presence of sulfuric acid (0.2 eqiuv) afforded 2-benzylsubstituted olefins **4** and **5** in moderate yields. The Baylis–Hillman adducts **3** were prepared from the corresponding *N*–tosylimine derivatives **2** [3–10] and activated vinyl compounds such as ethyl acrylate or acrylonitrile according to the literature methods [11–12].

In the reactions we could obtain 2–benzylsubstituted trisubstituted olefin derivatives **4** and **5**, which means that the reaction might proceed *via* SN2′ type process. We could not obtain any of the olefins that were produced by direct replacement of the sulfonamide group. It is interesting to note that the stereochemisrty of the produced olefins **4** and **5** differs markedly according to the electron withdrawing group of the Baylis–Hillman adducts **3**. Where the EWG is methoxycarbonyl and ethoxycarbonyl group, *E* form olefin **4** was obtained exclusively (see Table 1), while the corresponding *Z* form **5** was obtained in the case of nitrile derivative as shown in Scheme 1 [13]. The assignment of stereochemistry of **4–5** was based on their ^{13}C NMR spectra [14]. The characteristic benzyl carbon appeared in 30.82–33.19 ppm in **4aa–4ca**, while in 39.35–42.10 ppm in **5da–5dd**.

This remarkable discrepancy could be explained by the relative stabilities of the

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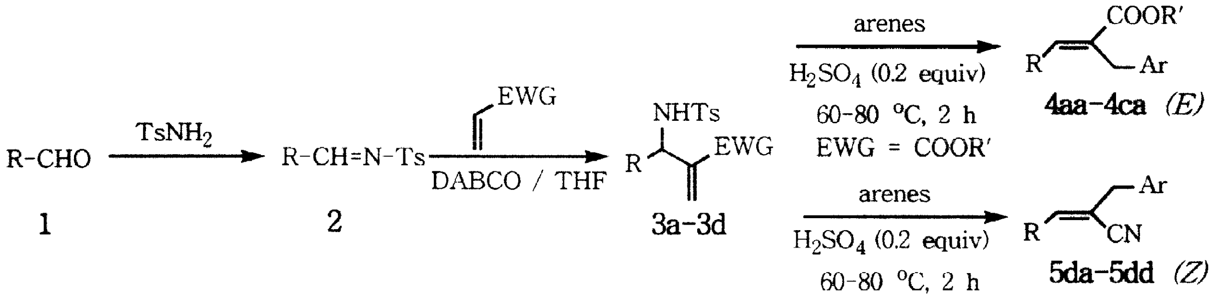


Scheme 1

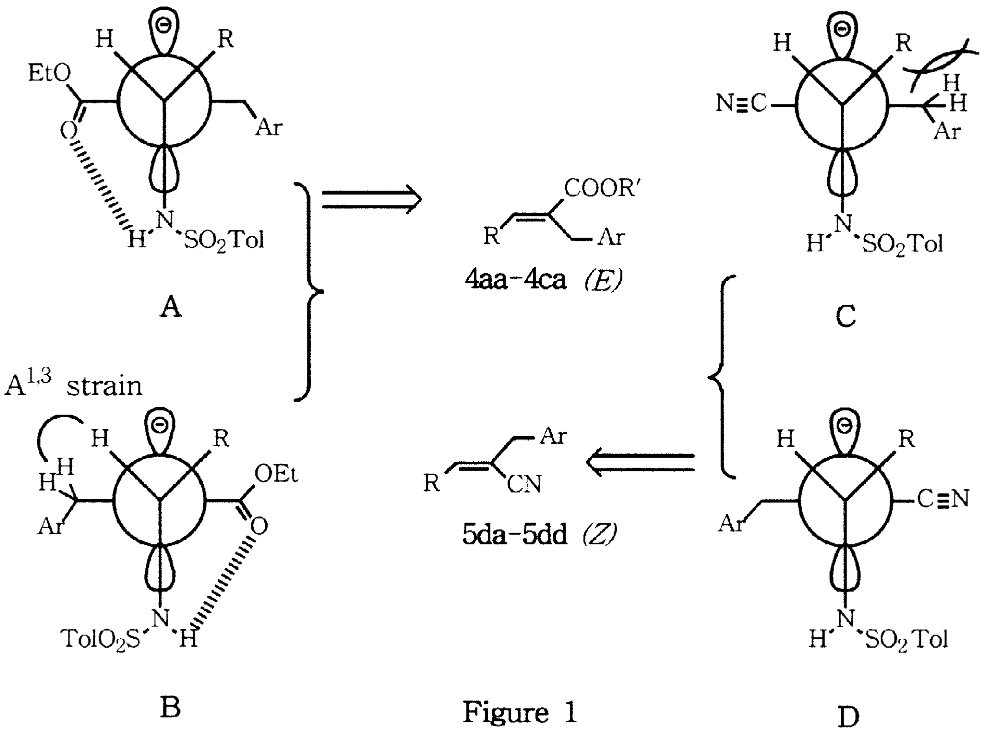
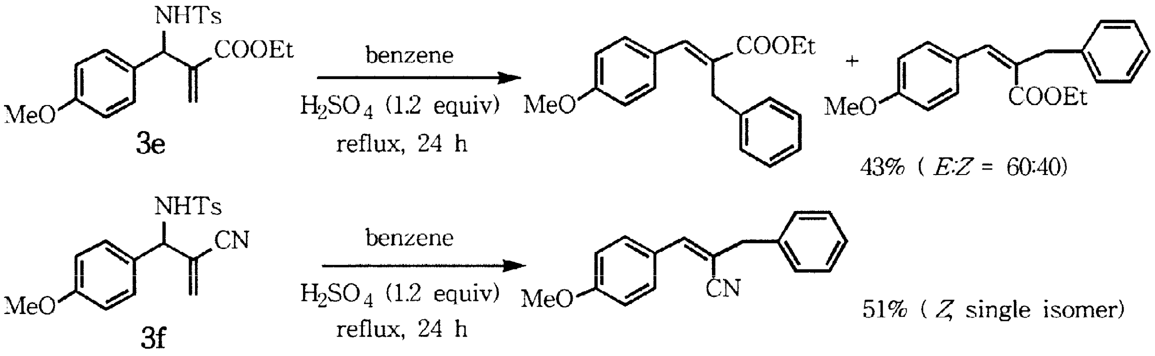
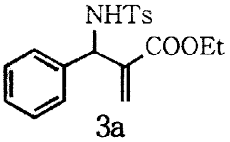
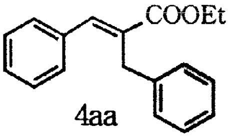
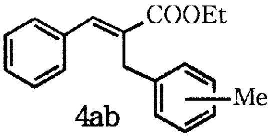
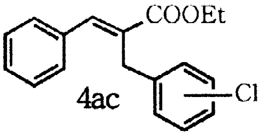
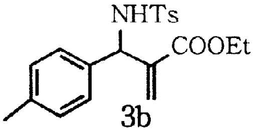
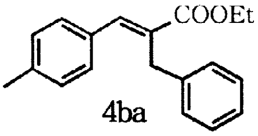
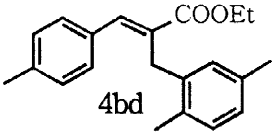
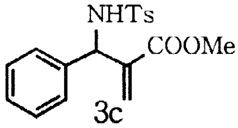
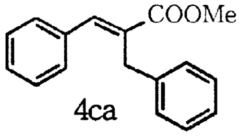
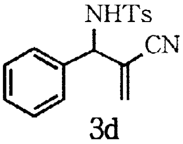
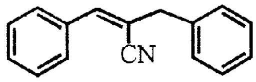
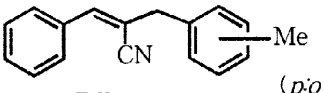
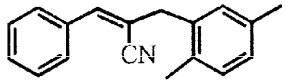


Figure 1



Scheme 2

Table 1. Synthesis of Stereodefined Trisubstituted Olefins 4-5.

entry	substrates	arenes	products[#]	yields (%)
1	 3a	benzene (a)	 4aa	74
2	3a	toluene (b)	 4ab	52 (p:o = 65:35)
3	3a	chlorobenzene (c)	 4ac	42 (p:o = 55:45)
4	 3b	benzene (a)	 4ba	50
5	3b	p-xylene (d)	 4bd	86
6	 3c	benzene (a)	 4ca	69
7	 3d	benzene (a)	 5da	96
8	3d	toluene (b)	 5db	49 (p:o = 65:35)
9	3d	p-xylene (d)	 5dd	76

[#] Trace amounts (2-5%) of olefin that have opposite stereochemistry were observed on ^{13}C NMR spectra in entries 1,5,6, and 7. In other cases there was no detectable isomer that has opposite stereochemistry.

intermediates and the corresponding transition states as shown in Figure 1. In the case where ester functionality is substituted there are two possible rotamers A and B. There is allylic 1,3-strain in rotamer B, and thus the stereochemistry of the produced olefins is *E* by elimination of the *p*-toluenesulfonamide *via* conformer A. The intramolecular hydrogen bonding between ethoxycarbonyl group and the sulfonamide group in B makes the allylic 1,3-strain more severe. Whereas nitrile is substituted (rotamers C and D), generally expected nonbonded interaction strain between aryl moiety R and benzyl group is the prominent steric strain to make the rotamer C's energy high. Thus, thermodynamically more stable *Z* olefin is obtained in this case. These explanations were further convinced by the reaction of benzene with *p*-methoxy derivatives **3e** and **3f** (Scheme 2) [15]. In the case of **3e** the stereoselectivity was disrupted and *Z* form was obtained in appreciable amounts (*E*:*Z* = 60:40). The formation of *Z* olefin might be due to the diminished intramolecular hydrogen bonding by protonation of the oxygen atom of the methoxy group of **3e** [15]. Moreover there was obtained only the corresponding *Z* olefin by using **3f** as starting material, which reflects the fact that in this case the nonbonded interaction strain is the principle factor to determine the stereochemistry as in **3d**.

In conclusion, we have developed an efficient method for the preparation of stereochemically defined trisubstituted olefins from the easily accessible Baylis-Hillman adducts of *N*-tosylimines. Further studies on the Friedel-Crafts reaction with the Baylis-Hillman adducts of tosylimines derived from aliphatic aldehydes, and of vinyl ketones or vinyl sulfones are currently undergoing.

References and Notes

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[13] As an example, ^{1}H and ^{13}C NMR spectral data of **4aa** and **5da** were as follows; **4aa**: ^{1}H NMR ($CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 3.95 (s, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 7.18-7.40 (m, 10H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.09, *33.11 (benzyl carbon)*, 60.82, 125.99, 127.89, 128.41, 128.48, 128.60, 129.08, 131.03, 135.35, 139.47, 140.52, 168.06. **5da**: ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 2H), 6.96 (s, 1H), 7.24-7.74 (m, 10H); ^{13}C NMR ($CDCl_3$) δ *42.06 (benzyl carbon)*, 110.63, 118.60, 127.25, 128.58, 128.70, 128.79, 128.81, 130.02, 133.44, 136.36, 143.96.

[14] In ^{13}C NMR spectra of trisubstituted olefins, the benzyl carbon *cis* to phenyl group appeared downfield compared with that of the *trans* form in general (see reference 14a). During the course of these studies Basavaiah and co-workers have published one report on the Friedel-Crafts reaction of the Baylis-Hillman adducts of aldehydes, and there reported similar ^{13}C NMR data (see reference 14b); (a) Funabiki T, Hosomi H, Yoshida S, Tarama K. J. Am. Chem. Soc. 1982;104:1560-1568. (b) Basavaiah D, Krishnamacharyulu M, Hyma RS, Pandiaraju S. Tetrahedron Lett. 1997;38:2141-2144.

[15] In the cases of **3e** and **3f** somewhat severe reaction conditions were needed to effect the reaction. This might be due to the preferential protonation at the methoxy group rather than at the tosylamide group, which makes protonation at the sulfonamide more difficult and also changes the extent of hydrogen bonding between the ester and sulfonamide functionality. In such a drastic reaction conditions, **3a** gave only the *E* product **4aa**. In addition, isomerization of **4aa** to the corresponding *Z* isomer was not observed in the same reaction conditions of **3e**-**3f**.