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Camphor-derived sulfonylhydrazines: catalysts for Diels–Alder cycloadditions

Yves Langlois *, Alain Petit, Pauline Rémy, Marie-Christine Scherrmann, Cyrille Kouklovsky

Laboratoire de Chimie des Procédés et des Substances Naturelles, UMR 8182, ICMMO, Université de Paris Sud, 91405 Orsay, France

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ABSTRACT

Camphor-derived sulfonylhydrazines proved to be very active for organocatalyzed Diels–Alder cycloadditions with cyclopentadiene. Good chemical yields and enantiomeric excesses up to 89% and 88% are obtained for *endo*/*exo* adducts.

Since the pioneering work of McMillan and co-workers,[1] the enantioselective organocatalytic Diels–Alder cycloadditions have been the topic of intense research developed in all fields of this reaction.[2–9] With the background of our previous experience of the use of camphor-derived chiral auxiliaries,[10] we selected camphor sulfonylhydrazine derivatives, which could be prepared from the relatively cheap camphorsulfonic acid available in both enantiomeric forms, as potential catalysts in aldol and Diels–Alder reactions. During the course of this study, Ogilvie demonstrated the usefulness of camphoric acid hydrazide derivatives in the organocatalyzed Diels–Alder cycloadditions[11] and published a remarkable study concerning the mechanism of the reaction.[11b,c] As demonstrated by this author, the rigidity of this new catalyst as well as the so-called α-effect[12] explained its reactivity and selectivity. The recent disclosure of camphorsulfonyl derivatives organocatalyzed Diels–Alder cycloadditions,[13] prompts us to present our own independent results in this field. According to Scheme 1, camphorsulfonyl hydrazone **4a** is prepared from (+)-camphorsulfonic acid **1** in almost quantitative yield in a sequence needing no intermediate purification by a modification of the previous synthesis.[14] Cyanoborohydride reduction of hydrazone **4a** afforded the anticipated hydrazine **5a** in 75% overall yield from **1**.[15]

The efficiency of this new candidate for the Diels–Alder organocatalysis was further evaluated. The use of methanol as solvent was precluded because, with α,β-unsaturated aldehydes, the corresponding acetal adducts were isolated at the end of the reaction.[1a] Screening of the best reaction conditions led us to select nitromethane as solvent and 0.5 N to 1 N perchloric acid to promote the intermediate iminium formation. Under these conditions, cycloaddition between cinnamaldehyde and cyclopentadiene in the presence of 10% catalyst **5a** afforded smoothly at room temperature the corresponding adducts as a 40/60 mixture of *endo*–*exo* isomers in 87% yield after 4 h.[16] However, a moderate enantioselectivity was observed (ee *endo*: 30; ee *exo*: 62) (Table 1, entry 1). After only 1 h, these adducts were still isolated in 81% yield, thus demonstrating the efficiency of the catalyst under these reaction conditions (entry 2).

In order to compare the enantiomerically enriched adducts with the racemic coumpounds, cycloadditions were also achieved under the same reaction conditions in nitromethane with *N*,*O*-dimethyl hydroxylamine hydrochloride **9** as catalyst. Thus, racemic adducts were isolated for comparison as carbonyl derivatives, which is not the case if methanol is used as solvent.[12a]

Introduction of a side chain at the *N*-sulfonyl nitrogen proved crucial to improve the enantioselectivity. Accordingly, hydrazone **4a** was in turn N-alkylated to furnish the substituted hydrazones **4b**–**e**. Despite numerous experiments, in our hands, the cyanoborohydride reduction of substituted hydrazones **4b**–**e** was never complete and the corresponding hydrazines **5b**–**e** were isolated along with starting material which was recycled (Scheme 1).[15] Cycloadditions with the benzyl-substituted hydrazine **5b** were achieved within 2 h in 73% yield and an increased enantioselectivity (ee *endo*: 87; ee *exo*: 85) (entry 3).

The absolute configuration of these *endo* and *exo* adducts was deduced after comparison by chiral GC analysis with the corresponding compounds obtained with the MacMillan catalyst.[1a] Thus, for the *endo* adduct, for instance, the same type of transition state model already proposed by Ogilvie and co-workers[11c] can be proposed for these cycloadditions (Fig. 1).

The amount of catalyst **5b** can be diminished to 2% and afforded after 16 h a mixture of adducts in 66% yield, however, with lower enantioselectivity (entry 5). With lower amount of catalyst (0.5%), both yield and enantioselectivity decreased dramatically (entry 6). The absence of any chiral induction for the *endo* isomer suggests that this compound could be the result of a cycloaddition catalyzed with perchloric acid (Scheme 2).

The influence of modifications of the benzyl unit on the reactivity and on the selectivity of the catalyst was then studied. Results are summarized in Table 1. With the 4-bromo benzyl derivative **5c** slightly better enantioselectivities were obtained (entry 7). However, introduction of electron-donating substituents in catalysts

* Corresponding author. Tel.: +33 1 69 15 76 30; fax: +33 1 69 15 46 79.
E-mail address: langlois@icmo.u-psud.fr (Y. Langlois).

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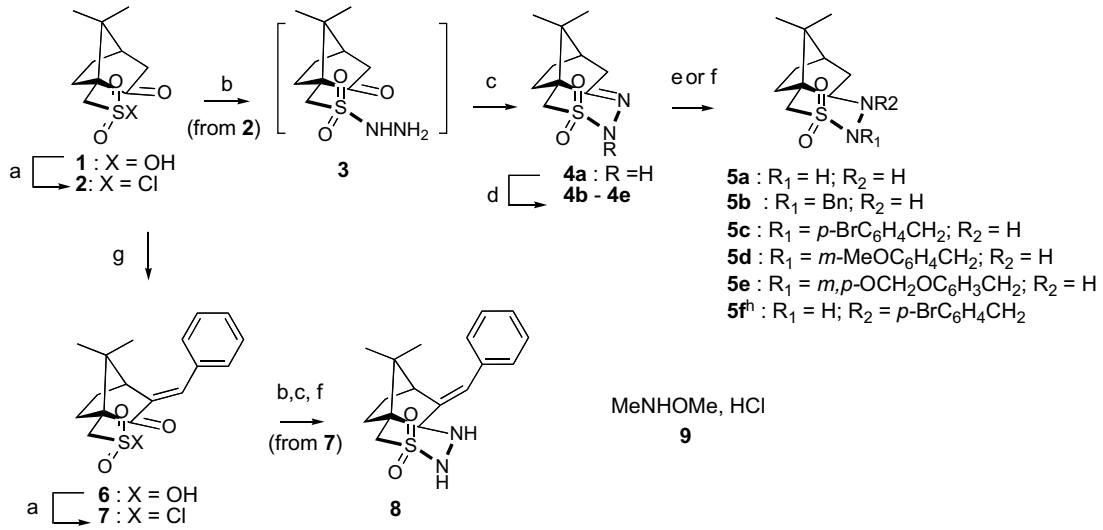
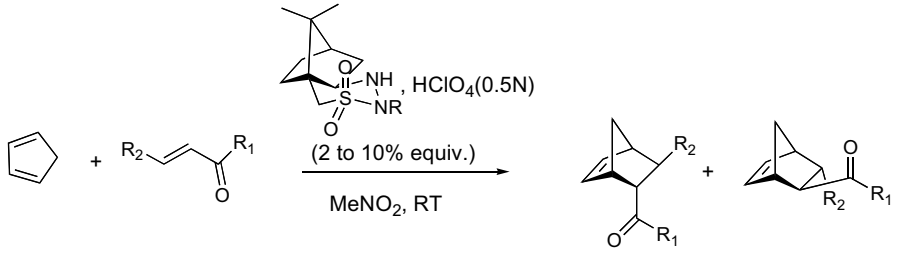


Scheme 1. Reagents and conditions: (a) $SOCl_2$ (neat), 80 °C, 3 h; (b) NH_2NH_2 (4 equiv), Et_3N, CH_2Cl_2, 20 h, rt; (c) PhMe, 80 °C, 3 h; (d) KHMDS, THF, $ArCH_2Br$, −78 °C to 20 °C, 20 h; (e) $NaBH_3CN$ (3 equiv), THF/MeOH, MeOH/HCl 1 N, 0 °C; (f) $NaBH_3CN$ (10 equiv), AcOH/MeOH, rt; (g) PhCHO (1,1 equiv), *t*BuOK (4 equiv), PhMe, 80 °C 20 h; (h) see Ref. 17.

Table 1
Cycloadditions between cinnamaldehyde and cyclopentadiene



Entry	Cat. (%)	Time (h)	Yield (%)	*endo*/*exo*[a]	ee (%) *endo*/*exo*[a]
1	**5a** (10)	4	87	40/60	30/62
2	**5a** (10)	1	81	40/60	n.d.[b]
3	**5b** (10)	2	73	40/60	87/85
4	**5b** (5)	2	51	50/50	72/82
5	**5b** (2)	16	66	56/44	46/70
6	**5b** (0.5)	5	20	70/30	0/40
7	**5c** (10)	20	52	50/50	89/88
8	**5d** (10)	36	32	60/40	20/82
9	**5e** (6)	24	60	65/35	26/88
10	**5f** (10)	48	11	93/7	0/0
11	**8** (5)	28	73	44/56	30/20
12	**9** (20)	24	32	36/64	—
13	None	26[c]	6	58/42	—

[a] Determined by GC with QC3/Cydex B, 25 m, OD 0.43 mm, film thickness 0.25 μ.
[b] Non-determined.
[c] Temperature 70 °C.

5d and **5e** which could stabilize the iminium intermediate maintains the same range of enantioselectivity for the *exo* isomer but decreased significantly the ee value for the *endo* isomers (entries 8 and 9). This observation is not easily rationalized. In contrast with the results observed by Lee and co-workers,[13] when the basic nitrogen is substituted in compound **5f**,[17] under our reaction conditions, racemic adducts were isolated in low yield (entry 10). We also examined the influence of introduction of an additional substituent in α to the basic nitrogen. Thus, crotonization between (+)-camphorsulfonic acid **1** and benzaldehyde gave benzylidene camphorsulfonic acid **6**.[18] After the same sequence of reactions, this compound afforded the anticipated benzylidene hydrazine derivative **8**. However, this catalyst gave disappointing results and the enantioselectivity was rather poor for both adducts (Table 1, entry 11).

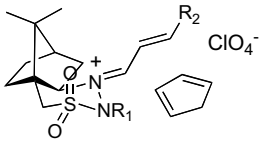
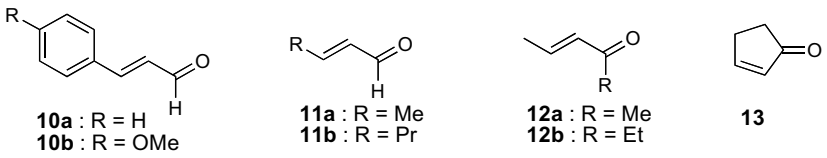


Figure 1.

Other Diels–Alder cycloadditions were subsequently examined with these catalysts with different α,β-unsaturated aldehydes and ketones. The results are summarized in Table 2. With the less



Scheme 2.

Table 2
Cycloadditions between dienophiles **10b**–**13** and cyclopentadiene

Entry	Cat. (%)	Dienophile	Time (h)	Yield (%)	*endo*/*exo*	ee (%) *endo*/*exo*
1	**5b** (10)	**10b**	24	68	42/58	—/78
2	**9** (20)	**10b**	36	10	54/46	—
3	**5b** (10)	**11a**	24	88	68/32	40/—
4	**9** (20)	**11a**	28	72	47/53	—
5	**5b** (10)	**11b**	20	95	74/26	26/42
6	**8** (5)	**11b**	24	67	70/30	0/0
7	**9** (20)	**11b**	20	57	60/40	—
8	**5a** (20)	**12a**	3	75	97/3	0/0
9	**5b** (5)	**12b**	24	56	95/5	0/0
10	**9** (20)	**12b**	20	90	94/6	—
11	**8** (5)	**12b**	20	96	95/5	0/0
12	**5a** (10)	**13**	5	28	93/7	34/—
13	**5b** (10)	**13**	20	62	95/5	0/—
14[a]	**5b** (10)	**10a**	2	73	40/60	87/85

[a] This experiment (Table 1, entry 3) has been added for comparison.

reactive *p*-methoxy cinnamaldehyde **10b**, catalyst **5b** gave significantly lower ee than with the unsusbstituted aldehyde **10a** (entry 1). In the aliphatic series with catalyst **5b** an increase of *endo*/*exo* ratio was observed but the enantioselectivity is dramatically reduced for both adducts (entries 3 and 5). With the benzylidene catalyst **8**, racemic adducts were isolated (entries 6 and 11).

With α,β-unsaturated ketones as dienophiles, only the Mac Millan catalyst[1b] has given good stereoselectivity in organocatalyzed Diels–Alder cycloadditions. It turned out that in our case, no enantioselectivity was observed. In contrast to the observation of Mac Millan,[1b] in our conditions, the use of hexenone **12b** instead of pentenone **12a**[19] did not improve the enantioselectivity (entries 8, 9, and 11). Nevertheless, high *endo* selectivity and often good yields were obtained (entries 8 and 9–11). The case of cyclopentenone **13** is not worthy, with catalyst **5a**, the *endo* adduct was obtained with 30% ee (entry 12) but with **5b**, the same adduct was found to be racemic.

In summary, under our reaction conditions, camphor-derived sulfonyl hydrazines, easily prepared from camphorsulfonic acid, showed to be very active organocatalysts in Diels–Alder cycloadditions. Racemic adducts were easily prepared for comparison with *N*,*O*-dimethyl hydroxylamine as catalyst. As often with other organocatalysts, the *endo*/*exo* selectivity as well as the enantioselectivity are difficult to be rationalized. *Endo* and *exo* adducts are probably obtained with different relative kinetic constants. Further studies towards the synthesis of supported camphor-derived organocatalysts are in current development.

Acknowledgments

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15. Preparation of compound **4a**: $SOCl_2$ (3.64 mL, 25 mmol) was added dropwise to crystalline (+)-camphorsulfonic acid **1** (4,64 g, 20 mmol) under argon. The

brown reaction medium was then heated at 80 °C for 3 h. The resulting brown slurry was poured into ice and then extracted with CH_2Cl_2 affording crude **2.** To a solution of NH_2NH_2 (64% in H_2O, 80 mmol, 4 mL) and Et_3N (80 mmol, 6 mL) in CH_2Cl_2 (50 mL) was added dropwise a solution of crude **2** (20 mmol) in CH_2Cl_2 (50 mL). The reaction medium was stirred for 20 h at room temperature, extracted with CH_2Cl_2, washed three times with H_2O and then with brine. After evaporation, the crude compound **3** was dissolved in toluene (20 mL) and heated at 80 °C for 3 h. Evaporation of solvent afforded compound **4a** (4,1 g, 90%). Compound **4a**: $[\alpha]_D^{22}$ −12 (*c* 1.47, $CHCl_3$); ^{1}H NMR 360 MHz, $CDCl_3$, δ, ppm, *J* Hz: 7.1 (s, 1H), 3.28 (d, *J* = 14, 1H), 3.16 (d, *J* = 14, 1H), 2.5 (m, 1H), 2.4 (m, 1H), 2.2–1.4 (m, 5H), 1.1 (s, 3H), 0.9 (s, 3H). ^{13}C NMR, 90 MHz, $CDCl_3$, δ, ppm: 165.1, 56.1, 49.3, 48.5, 45.6, 36.0, 31.4, 27.3, 20.0, 18.0. MS(ESI+) *m*/*z*: 251 (M+23), 228. Preparation of compound **5a**: To a cooled solution (0 °C) of **4a** (320 mg, 1.4 mmol) and small amount of methyl orange in THF/MeOH (50/50, 12 mL) was added $NaBH_3CN$ (210 mg, 3.3 mmol) portionwise in 1 h. The pH was maintained around 3.8 by the addition of a solution HCl/MeOH (1 N). After an additional hour, the reaction medium was extracted with CH_2Cl_2 and the organic layer was washed successively with H_2O/NH_4Cl, $H_2O/NaHCO_3$ and brine. After chromatography (SiO_2, heptane/AcOEt 50/50) compound **5a** was isolated in 83% yield. Compound **5a**: $[\alpha]_D^{22}$ −82 (*c* 1.3, $CHCl_3$); ^{1}H NMR 360 MHz, $CDCl_3$, δ, ppm: 5.5 (s, 1H), 4.2 (br s, 1H), 3.36 (d, *J* = 12, 1H), 3.12 (d, *J* = 12, 1H), 3.08 (m, 1H), 1.9–1.5 (m, 5H), 1.36 (s, 3H), 1.34–1.08 (m, 2H), 0.96 (s, 3H). ^{13}C NMR, 90 MHz, $CDCl_3$, δ, ppm: 63.0, 50.0, 49.5, 47.0, 45.8, 37.8, 34.0, 26.2, 21.2, 20.5. MS(ESI+) *m*/*z*: 253 (M+23), 230. Compounds **5b** and **5d** were prepared by reduction of **4b** and **4d** with the same protocol (**5b** 40%, recovery of starting material 47%; **5d**, 33%). Compounds **5c** and **5e** were prepared by $NaBH_3CN$ (10 equiv) reduction in AcOH/MeOH (2/1) according to Ref. 11a (**5c** 40%, **5e** 33%, SM 42%). Preparation of compound **4b**: To a solution of **4a** (456 mg, 2 mmol) in THF (10 mL) under argon at −78 °C was added dropwise a solution of KHMDS (0.5 M in toluene, 2.2 mmol, 4.4 mL). The temperature of the reaction medium was leaf to raise to 0 °C in 30 min and recooled to −78 °C. BnBr (240 μL, 2 mmol.) was then added dropwise and the reaction was stirred at room temperature for 16 h. Reaction medium was extracted with CH_2Cl_2, washed successively with aqueous $NaHCO_3$ (5%) and brine. The crude product was purified by SiO_2 chromatography (heptane/*t*BuOMe 60/40) affording **4b** (570 mg, 89%). $[\alpha]_D^{22}$ −80 (*c* 0.95, $CHCl_3$); ^{1}H NMR 360 MHz, $CDCl_3$, δ, ppm: 7.6–7.2 (m, 5H), 4.9 (d, *J* = 14, 1H), 4.6 (d, *J* = 14, 1H), 3.2 (d, *J* = 14, 1H), 3.1 (d, *J* = 14, 1H), 2.6–2.5 (2t, 1H), 2.5–2.3 (m, 1H), 2.1–1.3 (m, 4H), 0.9 (s, 3H), 0.8 (s, 3H). ^{13}C NMR, 75 MHz, $CDCl_3$, δ, ppm: 165.3, 136.5, 129.9, 128.6, 127.5, 56.0, 53.0, 49.0, 48.5, 44.0, 36.2, 31.0, 27.0, 19.8, 18.0. MS(ESI+) *m*/*z*: 341 (M+23), 318. Compound **5b**: $[\alpha]_D^{22}$ −80 (*c* 1.05, $CHCl_3$); ^{1}H NMR 360 MHz, $CDCl_3$, δ, ppm: 7.5–7.2 (m, 5H), 4.6 (d, *J* = 14, 1H), 4.1 (d, *J* = 14, 1H), 3.4 (d, *J* = 14, 1H), 3.2 (d, *J* = 14, 1H), 3.2 (m, 1H), 1.8–1.4 (m), 1.35 (s, 3H), 1.4–1 (m, 2H), 0.95 (s, 3H). ^{13}C NMR, 90MHz, $CDCl_3$, δ, ppm: 136, 128.6, 128.3, 127.6, 62.5, 51.3, 50.7, 50.4, 46.7, 45.2, 37.1, 34.2, 25.9, 21.1, 20.6. MS(ESI+) *m*/*z*: 321 (M+1).

16. Typical experiment for cycloaddition: To a solution of catalyst **5b** (16 mg, 0.05 mmol) in nitromethane (900 μL) was added successively, $HClO_4$ (0.5 N, 1 equiv, 100 μL), aldehyde (0.5 mmol) and cyclopentadiene (1.5 mmol) under argon. The reaction medium was vigourously stirred at room temperature and the reaction was monitored by TLC (SiO_2, heptane/*t*BuOMe: 80/20 to 60/40). At the end of the reaction, the reaction medium was poured in CH_2Cl_2, washed with aqueous $NaHCO_3$ (5%) and brine. After drying over $MgSO_4$, filtration and evaporation, the crude mixture was purified by preparative TLC.
17. Compound **5f** was prepared by alkylation of compound **5a** with *p*Br-$C_6H_4CH_2Br$ after deprotonation with KHMDS.
18. (a) Bouillon, C.; Vayssie, C.; Richard, F. U.S. Patent 1,165,336, 1982.
19. Racemic adduct (entry 8) was prepared according to: Stork, G.; Guthikonda, R. N. *Tetrahedron Lett.* **1972**, *27*, 2755–2758.