Supporting Information

An Unexpected Diethyl Azodicarboxylate-promoted Dehydrogenation of Tertiaryamine and Tandem Reaction with Sulfonyl Azide

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Caution: Azides and diazoalkanes may be hazardous and/or explosive.

Experimental Section

All reactions were carried out using standard Schlenk techniques. CH₃CN was dried over CaH₂. Et₃N and 1,4-dioxane were distilled from sodium/benzophenone. Substituted sulfonyl azides were prepared according to literature.¹ Tri-*n*-butylamine and tri-*n*-hexylamine were purchased from Sigma-Aldrich company. ¹H and ¹³C NMR spectra were recorded at room temperature in CDCl₃ or DMSO-d₆ on Bruker AMX-500 MHz instrument with TMS as internal standard. Coupling constants are reported in Hertz (Hz). GC-MS spectra were performed on a Agilent GC-6890, MS-5973 instrument.

1. Procedure for the capture of vinyldiethylamine by chalcone: To a 10 mL two-necked round-bottom flask with a mixture of chalcone (0.208 g, 1mmol) and DEAD (0.471 mL, 3 mmol) in anhydrous 1,4-dioxane (3 mL) was added triethylamine (0.42 mL, 3 mmol). The resulting mixture was stirred for 1 hour at 10-15°C, then at ambient temperature (about 25-30°C) for 8 h. The mixture was treated with 5 mL saturated NH₄Cl and 20 mL water, then extracted with diethyl ether 3x30 mL, washed with water 2x20 mL, dried with anhydrous MgSO₄, filtered and evaporated under reduced pressure to give crude product. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (8:1-5:1) as eluent to give the pure product. 0.088 g, 35% yield.

$$\begin{array}{c|c} Ph & + & Et_3N + DEAD \\ \hline O \end{array} \xrightarrow{(1) 1,4-dioxane} & Ph \\ \hline (2) H^+/H_2O \end{array} \xrightarrow{Ph} \\ O \\ CHO \end{array}$$

¹H NMR (500 MHz, CDCl₃)² δ = 2.79-2.85 (m, 1H), 2.89-2.94 (m, 1H), 3.40-3.46 (m, 2H), 3.95-4.01 (m, 1H), 7.19-7.32 (m, 5H), 7.43-7.46 (m, 2H), 7.54-7.57 (m, 1H), 7.90-7.92 (m, 2H), 9.71 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ = 35.4, 45.0, 49.6, 127.0, 127.4, 128.1, 128.6, 128.8, 133.3, 136.8, 143.2, 198.1, 201.2.

2. Procedure for the capture of diazomethane, diazopropane, and diazopentane: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL) was added triethylamine, (or tri-*n*-butylamine, or tri-*n*-hexylamine) (1 mmol). The resulting mixture was stirred for 0.5 h at 10-15°C, then benzoic acid (0.122 g, 1 mmol) was added and stirred at 10-15°C for 2 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (10:1-8:1) as eluent to give the pure product. The methyl benzonate, propyl benzonate, or pentyl benzonate was identified by NMR and/or GC-MS.

$$p\text{-}\mathsf{TsN}_3 + \mathsf{DEAD} + \begin{cases} n\text{-}\mathsf{HexyI_3N} \\ n\text{-}\mathsf{Bu_3N} \\ \mathsf{Et_3N}, \end{cases} \underbrace{(1) \ 1, 4\text{-}\mathsf{dioxane}}_{\mathsf{CH}_2\mathsf{N}_2} & \begin{cases} n\text{-}\mathsf{PentyIN}_2 \\ n\text{-}\mathsf{PrN}_2 \\ \mathsf{CH}_2\mathsf{N}_2 \end{cases} \xrightarrow{\mathsf{PhCOOH}} \begin{cases} \mathsf{PhCOO(CH_2)_4CH_3} \\ \mathsf{PhCOOPr}^n \\ \mathsf{PhCOOPr}^n \\ \mathsf{PhCOOMe} \end{cases}$$

NMR of methyl benzonate: ¹H NMR (500 MHz, CDCl₃) δ = 3.92 (s, 3H), 7.42-7.45 (t, *J* = 7.5 Hz, 2H), 7.54-7.57 (m, 1H), 8.03-8.05 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ = 52.1, 128.3, 129.6, 130.2, 132.9, 167.1.

Procedure for the isolation of 2H-DEAD: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous CH₃CN (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C) for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure 2H-DEAD. 0.154 g, 87% yield. ¹H NMR (500 MHz, DMSO-d₆) δ = 1.16-1.19 (t, *J* = 7.0 Hz, 6H), 4.01-4.06 (g, *J* = 7.0 Hz, 4H), 8.97 (s,

2H); 13 C NMR (125 MHz, DMSO-d₆) δ = 15.0, 60.9, 157.0.

Reference:

- 1. Regitz, M.; Hocker, J.; Liedhegener, A. Org. Synth. 1973, 48, 36.
- 2. Mukaiyama, T.; Yanagisawa, M.; Iida, D.; Hachiya, I. Chem. Lett. 2000, 6, 606.





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GC-MS: PhCOOMe







 $m \ /z \longrightarrow$

GC-MS: PhCOOCH₂CH₂CH₃

Abundance



GC-MS: PhCOO(CH₂)₄CH₃



Abundance

