

Copper(II)-catalyzed aerobic oxidation of hydrazides to azo intermediates and their Diels–Alder *versus* ene trapping

Duangduan Chaiyaveij^{a*} and Andrew Whiting^{b*}

^aChemistry Department, Faculty of Science and Technology, Thammasat University, Khlong Luang, Pathum Thani, 12120, Thailand

^bCentre for Sustainable Chemical Processes, Department of Chemistry, Durham University, Science Laboratories, South Road, Durham, DH1 3LE, UK

Email: chaiyavech@hotmail.com; andy.whiting@durham.ac.uk

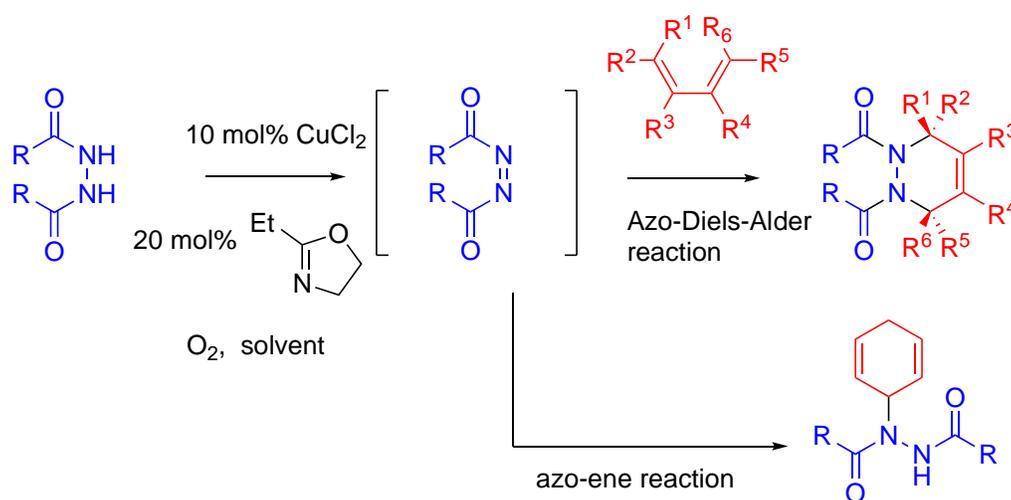
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Abstract

The oxidation of diethyl 1,2-hydrazinedicarboxylate using a catalytic Cu(II)-oxazoline system occurs at RT in air, resulting in azo generation, which can then be trapped *in situ* via hetero-Diels-Alder (HDA) and competitive ene-reactions, with chemoselectivity being both temperature and solvent dependent. The procedure was extended to other azo systems and mechanism studies are reported.



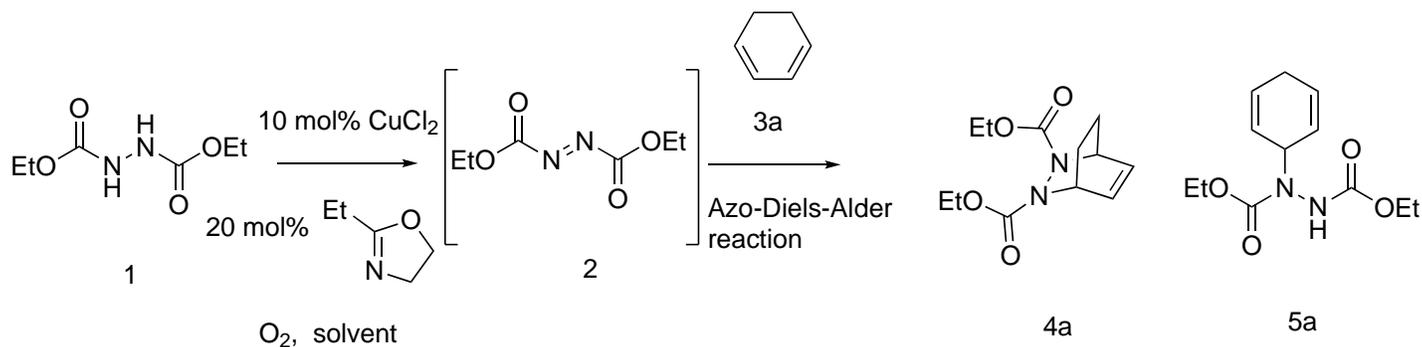
Keywords: Hetero-Diels-Alder reaction, azo, ene-reaction, copper(II)-catalyzed aerobic oxidation

Introduction

The reaction of azo dienophiles with conjugated dienes *via* a [4+2]-cycloaddition is over a century old¹⁻³ and it was one of first examples of a hetero-Diels-Alder (HDA) reaction. This reaction has been used extensively in organic synthesis as a powerful synthetic route to 1,4-diamines,^{4,5} which are biologically active compounds present in many protease inhibitors;^{6,7} and have potential for the preparation of antitumor agents.⁸ The formation of azo dienophiles from hydrazines employs harsh conditions, e.g. fuming HNO₃ or oxidation by using halogens,^{9,10} and hence, there is a need to develop mild, clean, sustainable catalytic conditions for the oxidation of hydrazines directly to azo compounds. This system is very similar to the generation of diimide from hydrazine with molecular oxygen.¹¹ We set out to develop new methods to achieve this reaction, preferably developing conditions where the oxidant was air. Indeed, our previous work reported a CuCl₂-2-ethyl-2-oxazoline catalytic system which operated at RT and oxidized hydroxamic acids to acyl nitroso species, which were trapped *in situ* by various dienes (the intermediate nitroso species were not isolable).^{12,13} We therefore hypothesized that this system might also be applicable to the oxidation of hydrazines to the corresponding azo species, since acylhydrazides are expected to be directly analogous to hydroxamic acids and should oxidize similarly. An initial demonstration of this was exemplified by generating an azo compound that was directly trapped intramolecularly by a diene *in situ* in excellent yield.^{12,13} Although it has been recently shown that certain copper complexes can be used as mild oxidation systems for a number of related reactions,¹⁴⁻²⁰ the copper-catalyzed aerobic oxidation of hydrazines and hydrazides to the corresponding azo compounds remains largely unexplored, with one example back in 1948²¹ using catalytic CuBr and *di-tert* butyldiaziridinone as oxidant was reported, however, the resulting azobenzene did not undergo HDA trapping.²² It has also been recently reported that a CuI-DMAP system oxidizes *di-tert*-butylhydrazodicarboxylate to the corresponding azodicarboxylate which was used *in situ* to dehydrogenate 1,2,3,4-tetrahydroquinolines.²³ However, these oxidation conditions were not suitable for the *in situ* hetero-Diels-Alder reaction. There is, therefore, a clear need to develop an efficient, general, robust, clean, aerobic and catalytic oxidative route to azo compounds directly from hydrazides, and herein, we report the use of a CuCl₂-2-ethyl-2-oxazoline catalyst system for this oxidation which is diene compatible, allowing efficient HDA trapping *in situ*.

Results and Discussion

The reaction of diethyl azodicarboxylate (DEAD) with 1,3-cyclohexadiene is known to result in competing outcomes through HDA and ene pathways²⁴⁻²⁷ forming two products, i.e. **4a** and **5a**. Initial attempts at developing an aerobic oxidation of hydrazine **1** were focused upon this reaction to examine the HDA:ene ratio in various solvents, as shown in Scheme 1 and corresponding results in Table 1.



Scheme 1. Azo-dienophile generation and trapping with cyclohexadiene.

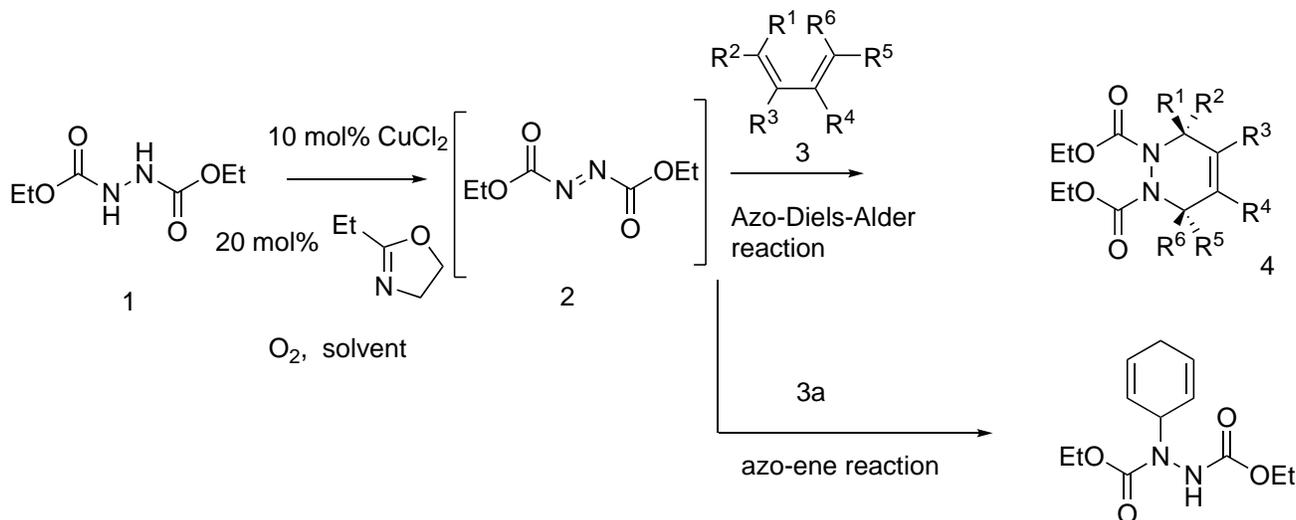
Table 1. Solvent effects for the aerobic oxidation of **1** followed by trapping with **3a**

Entry	Solvent	Temp. (°C)	Time (h)	Ratio ^a 4a : 5a	Yield ^b (%)
1	MeOH ^{a,c}	rt	240	29:71	7
2	MeCN ^b	rt	96	36:64	56
3	EtOH ^{a,c}	rt	240	32:68	5
4	EtOAc ^{a,c}	rt	240	35:65	10
5	Toluene ^b	reflux	6	74:26	87
6	MeOH:Toluene, 1:4 ^{a,c}	rt	240	45:55	4
7	CHCl ₃ ^{*a}	rt	48	29:71	86

^aIntegration at using the signals at 6.70-6.45 to 5.94 (=C-H resonances in **4b** and **5b** respectively).

^bIsolated yield after purification (see Supporting Information).

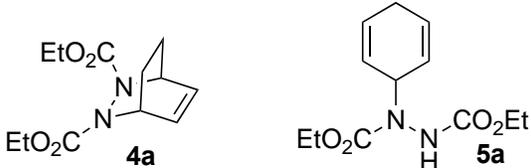
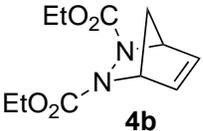
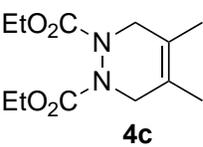
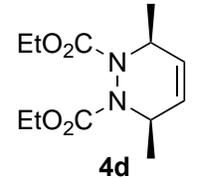
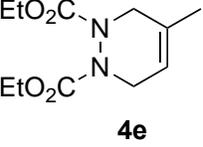
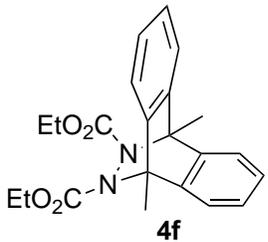
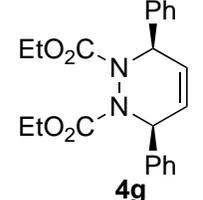
The results from Table 1 clearly show that the ratio between cycloadduct **4a** and ene product **5a** varied as a function of solvent. Reactions carried out in MeOH and CHCl₃ gave more ene adduct **5a** compared to cycloadduct **4a** (71:29, Entries 1 and 7, Table 1), whereas in toluene (reflux), more cycloadduct **4a** than ene **5a** (74:26) was observed and the reaction finished in 6 h (Entry 5, Table 1). However, even though MeOH gave good ene to HDA selectivity, the yield was poor (7%) and the reaction failed to go to the completion. The reaction in MeCN (reflux) gave good HDA chemoselectivity in the nitroso system,^{12,13} but was considerably less selective in the azo application, giving only a 36:64 ratio of cycloadduct **4a** to ene **5a**. EtOH, EtOAc and a mixed solvent of MeOH/toluene (1:4) all gave reactions which did not complete even after 10 d. These reactions showed that the two best solvent systems were CHCl₃ (RT) and toluene (reflux), since both of these reactions (Entries 7 and 5, Table 1) resulted in good yields and chemoselectivities. The higher temperature toluene conditions particularly gave the HDA adduct with superior selectivity over the CHCl₃ conditions. After optimization of the solvent/reaction conditions, various dienes were then tested using the two main methods developed, as shown in Scheme 2 and Table 2



Scheme 2. Azo-dienophile generation and trapping with various dienes.

It is interesting to note from Table 2, that the chemoselectivity of the azo dienophile reaction in general with different dienes differed from that found previously with the nitroso systems.^{12,13} For example, for the nitroso reaction with 1,3-cyclohexadiene, no ene product was observed and only HDA was obtained. In contrast, in the azo system, there was both ene and HDA adducts were obtained (Entry 1, Table 2). Also, in the nitroso system,^{12,13} isoprene and 2,3-dimethyl-1,3-butadiene gave both ene and HDA products, whereas in the azo system, the ene products were not observed (Entries 5 and 3, Table 2). For 10-dimethylantracene and 1,4-diphenyl-but-1,3-diene (CHCl₃ RT), neither reaction went to completion, even after 10 and 15 d, respectively. Also, reaction times varied from 6-96 h, which shows that the oxidation was slower than the nitroso system. However, when these reactions were carried out in toluene (reflux), they completed in 96 h, giving 30 and 47% yields, respectively. In fact, the reaction in toluene generally gave better yields and was significantly faster than in CHCl₃, except for cyclopentadiene where the yield was poor due to the competing dimerization of the cyclopentadiene at the higher temperature (Entry 1, Table 2). Interestingly, all the azo cycloadducts in Table 2 when initially analyzed in CDCl₃ by ¹H NMR at RT, all the spectra were not easily interpreted due to the broadness and complexity of the signals. Hence, higher temperatures (25-80 °C) in *d*₆-DMSO were required to allow sharper spectra to be obtained (see Figure 1 for 4c, for example).

Table 2. Products and isolated yields for the *in situ* azo dienophile generation and Diels-Alder vs. ene trapping

Entry	Diene	HDA adducts 4 and ene-products 5	Solvent			
			CHCl ₃		Toluene	
			Time (h)	Yield % ^a (crude ratio of 4:5)	Time (h)	Yield % ^a (ratio 4:5)
1	Cyclohexa-1,3-diene 3a		48	86 (29:71) ^b	6	87(74:26) ^b
2	Cyclopentadiene 3b		48	92 ^c	96	10 ^c
3	2,3-Dimethylbuta-1,3-diene 3c		40	90 ^b	10	98 ^b
4	Hexa-2,4-diene 3d		48	74 ^b	6	94 ^b
5	2-Methylbuta-1,3-diene 3e		48	57 ^d	15	78 ^d
6	9,10-Dimethylanthracene 3f		240	17 ^{e,f}	96	30 ^{e,f}
7	1,4-Diphenylbuta-1,3-diene 3g		360	20 ^{f,g}	96	47 ^{f,g}

^aIsolated yields after purification (see Supporting Information). ^bSee references 24-27. ^cSee references 28,29.

^dSee reference 30. ^eSee reference 31. ^fThe ratio between **1** and diene was 1:1. ^gSee reference 32.

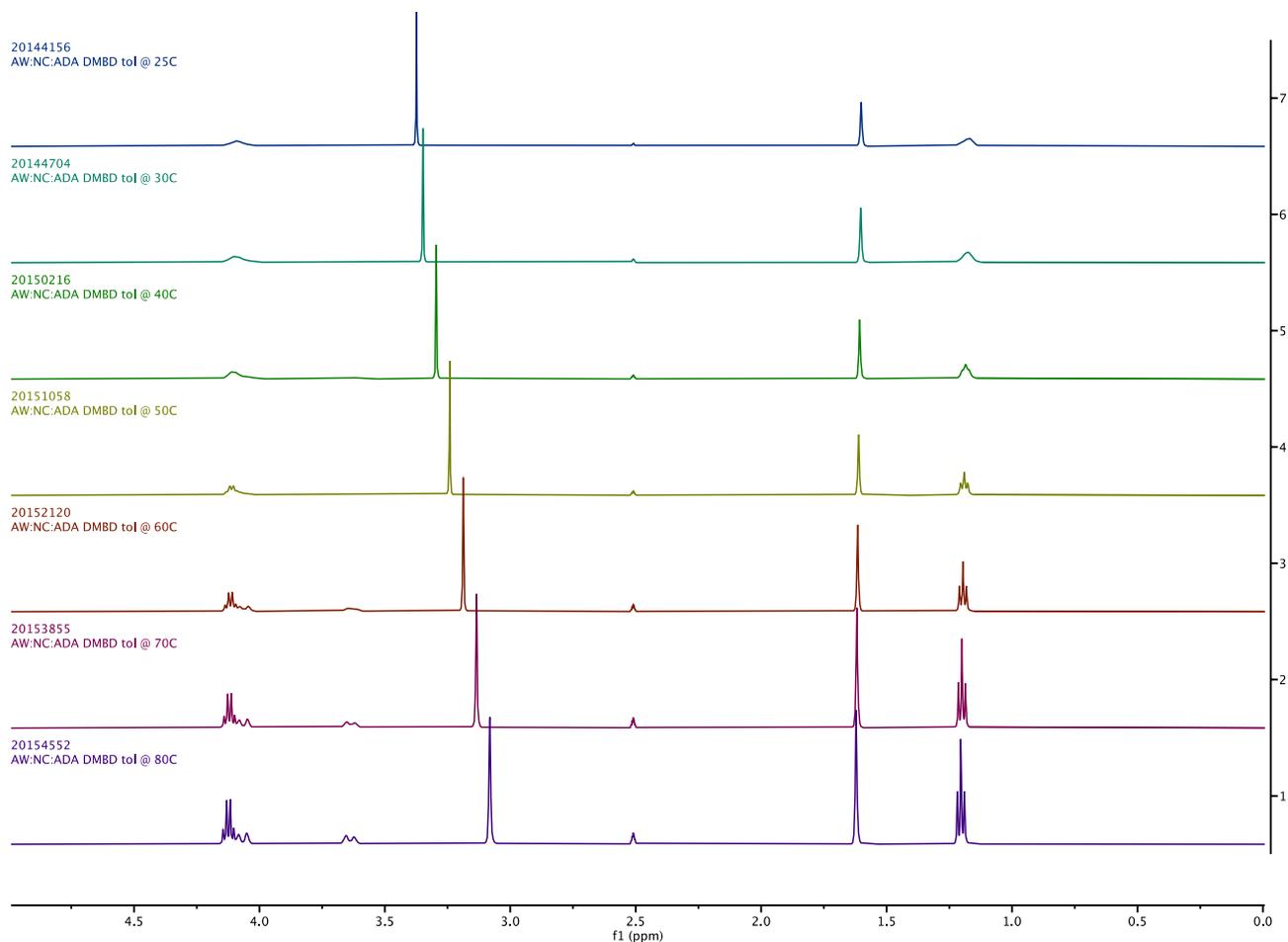
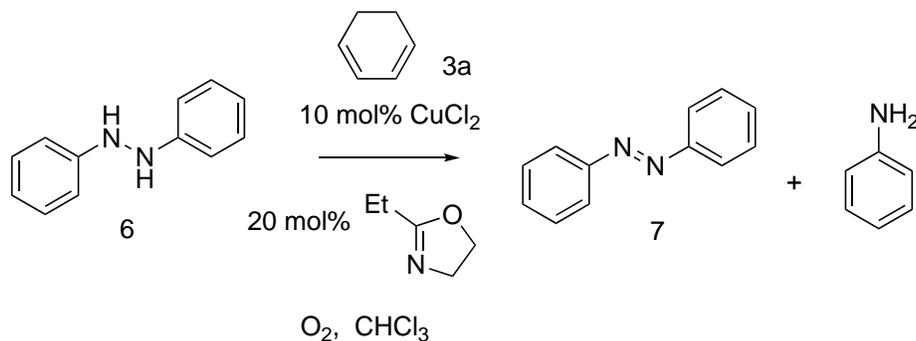


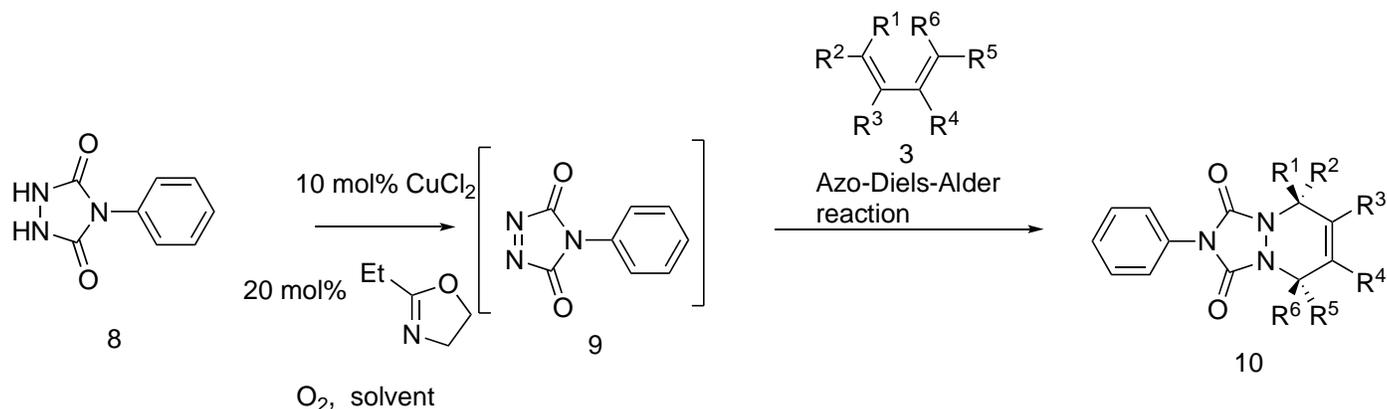
Figure 1. ¹H NMR of the cycloadduct **4c** in *d*₆-DMSO at various temperatures.

Having shown that the azo dicarboxylate system could be generated *in situ* (Table 1), other hydrazine analogues were examined. Firstly, applying the optimized conditions on 1,2-diphenylhydrazine **6** reacting with 1,3-cyclohexadiene (Scheme 3), no cycloadduct was observed from azo trapping by cyclohexadiene. Indeed, after 45 mins, azobenzene **7** was obtained (86%) together with small amounts of aniline.³³ This reaction shows that the azo compound was generated under the reaction conditions, but azo benzene is a poor dienophile, and does not trap efficiently.⁹ Also, aniline formation suggested that after the azo-benzene is formed, it is then reduced. Moreover, aniline can react with Cu(I) to form the azo compound.³⁴ Hence, we examined diethyl hydrazinedicarboxylate **1** without diene present under the same conditions but there was no azo compound **2** produced according to TLC and starting material was recovered.



Scheme 3. Attempts to oxidise diphenylhydrazine and trap with cyclohexadiene.

Next, the optimized catalytic conditions were employed on a system which might be more amenable to azo-formation and HDA trapping, i.e. the *in situ* oxidation of 4-phenylurazole (**8**) to 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**9**) which was trapped by various dienes to yield the cycloadducts **10** (Table 3).

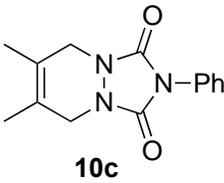
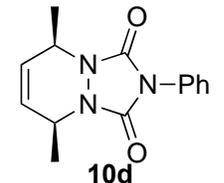
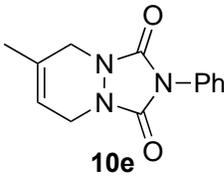
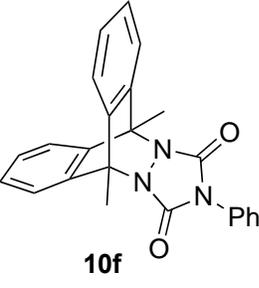
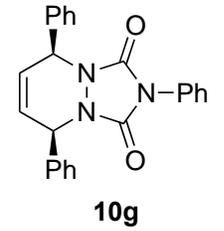


Scheme 4. Application of the oxidation-trapping sequence on 4-phenylurazole.

Table 3. *In situ* azo generation and Diels-Alder trapping

Entry	Diene	HDA adduct 10	Solvent	Time (h)	Yield (%) ^a
1	Cyclohexa-1,3-diene 3a		CHCl ₃	6	94 ^{b,c}
		10a	MeOH	5	96 ^{b,c}
2	Cyclopenta-diene 3b		CHCl ₃	5	94 ^b
		10b	MeOH	5	96 ^b

Table 3. Continued

Entry	Diene	HDA adduct 10	Solvent	Time (h)	Yield (%) ^a
3	2,3-Dimethyl-buta-1,3-diene 3c	 10c	CHCl ₃	8	98 ^b
			MeOH	7	98 ^b
4	Hexa-2,4-diene 3d	 10d	CHCl ₃	8	93 ^d
			MeOH	7	95 ^d
5	2-Methyl-buta-1,3-diene 3e	 10e	CHCl ₃	8	96 ^b
			MeOH	8	96 ^b
6	9,10-Dimethylantracene 3f	 10f	CHCl ₃	3	96 ^{e,f}
			MeOH	2	97 ^{e,f}
7	1,4-Diphenyl-buta-1,3-diene 3g	 10g	CHCl ₃	24	95 ^b
			MeOH	72	94 ^b

^aIsolated yields after purification. ^bSee reference 35. ^cSee reference 36. ^dSee reference 37. ^eSee reference 38. ^fSee reference 39.

The results in Table 3, showed that the oxidation of 4-phenyl urazole **8** to PTAD **9** using the Cu-oxazoline system worked well in both chloroform and methanol. The yield of cycloadducts was universally high (93-98%) and the reaction time varied from 2-72 hours. The reaction of **8** with diene **g** in methanol took the longest time to finish (Table 3, entry 7). This was due to the poor solubility of the

diene in methanol. However, diene **3f** was not sufficiently soluble in methanol, the reaction time was only 2 hours (Table 3, entry 6). The cycloadduct from this reaction was insoluble in methanol, therefore, the purification was a simple filtration.

Conclusions

An efficient, mild and green catalytic aerobic oxidation of hydrazide to azo derivative has been developed. This method can generate azo compounds *in situ*, which are readily trapped by a diene present in the reaction to form the corresponding cycloadducts in low to excellent yields depending upon the nature of the diene. The chemoselectivity of this reaction depends upon the reaction conditions and solvent. The reaction in toluene under reflux gave the best cycloadduct selectivity, whereas the reaction in chloroform gave the best ene selectivity.

Experimental Section

General. Reactions were performed in the presence of air. All reagents were purchased from Aldrich and used as received. Solvents (AR grade) were used as received. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ spectra were recorded using a Bruker Avance 400 operating at 400 MHz for ^1H NMR and ^{13}C NMR at 101 MHz, or for ^1H NMR recorded at 500 MHz using a Bruker DRX 500 spectrometer. CDCl_3 and d_6 -DMSO were used as the solvent for all samples. ^1H NMR chemical shifts are reported with reference to TMS using residual proton on non deuterated solvent (CDCl_3 : 7.26 ppm) whereas ^{13}C NMR spectra are reported with reference to TMS using the carbon signals of the deuterated solvent (CDCl_3 : 77.23 ppm). Elemental analysis was performed using an Exeter Analytical E440 machine by departmental service at Durham University. All chromatography was carried out using silica gel (Silicagel LC60A 40-63 μm) which obtained from Fluorochem. The removal of solvent was performed on a rotary evaporator in vacuum. IR spectra were recorded with a Perkin-Elmer 1615 FTIR spectrometer. Melting points were determined using an Electrothermal melting point apparatus. Low resolution mass spectrometry was carried out on a Waters TQD equipped with Acquity UPLC and an electrospray ion source and high resolution mass spectrometry on a Waters LCT Premier XE equipped with Acquity UPLC and a lock-mass electrospray ion source.

General procedure for solvent screening for the *in situ* azo-generation-Diels-Alder reaction using diethyl hydrazinedicarboxylate and trapping with 1,3-cyclohexadiene (Table 1). To 20 mL of solvent, 2.30 mmol of 1,3-cyclohexadiene, 10 mol % CuCl_2 and 20 mol % 2-ethyl-2-oxazoline was added, followed by 1.15 mmol of diethyl hydrazinedicarboxylate **1**. The resulting solution was stirred at room temperature in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The solvent was removed by evaporation and the crude product was purified by silica gel chromatography (hexane: ethyl acetate, 4:1 v/v as the eluent).

General procedure for the *in situ* azo-generation-Diels-Alder reaction using diethyl hydrazinedicarboxylate with various dienes in chloroform (Table 2). To a CHCl_3 (20 ml) solution of 2.30 mmol of appropriate diene, 10 mol % CuCl_2 and 20 mol % 2-ethyl-2-oxazoline was added 1.15 mmol of diethyl hydrazinedicarboxylate **1**. The resulting solution was stirred at room temperature in air and was monitored by TLC. The completion of the

reaction was confirmed by the disappearance of the starting material. The solvent was removed by evaporation and the crude product was purified by silica gel chromatography (hexane: ethyl acetate, 4:1 v/v as the eluent).

Example procedure for the *in situ* azo-generation-Diels-Alder reaction using diethyl hydrazinedicarboxylate with various dienes in toluene under reflux. To a toluene (20 ml) solution of 1,3-cyclohexadiene (188 mg, 2.35 mmol), CuCl₂ (16 mg, 0.12 mmol) and 2-ethyl-2-oxazoline (24 mg, 0.24 mmol) was added diethyl hydrazinedicarboxylate (207 mg, 1.18 mmol). The resulting solution was stirred under reflux in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The reaction was stirred for 6 h. The solvent was removed by evaporation and the crude product was purified by silica gel chromatography (hexane: ethyl acetate, 4:1 v/v as the eluent), giving **4a** (192 mg, 64%) and **5a** (68 mg, 23%). The ratio of **4a** to **5a** was determined on the crude product by ¹H NMR using the signals at δ 6.70-6.45 to 5.94 (=C-H resonances in **4a** and **5a** respectively). Analytical and spectroscopic data were identical to those reported in the literature.^{1,24,25}

Procedure for the azo-generation reaction using 1,2-diphenylhydrazine in chloroform. To a CHCl₃ (20 ml) solution of CuCl₂ (34 mg, 0.25 mmol) and 2-ethyl-2-oxazoline (50 mg, 0.50 mmol) was added 1,2-diphenylhydrazine (463 mg, 2.51 mmol). The resulting solution was stirred at RT in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The reaction was stirred for 45 minutes. The solvent was removed by evaporation and the crude product was purified by silica gel flash chromatography (hexane: ethyl acetate, 1:1 v/v as the eluent), giving **7** as orange solid (394 mg, 86%); mp 74-75.5 °C (lit. 66-67.5 °C). Analytical and spectroscopic data were identical to those reported in the literature^{40,41}

General procedure for the *in situ* azo-generation-Diels-Alder reaction using 4-phenylurazole with various dienes in chloroform (Table 3). To a CHCl₃ (20 ml) solution of the appropriate diene, 10 mol % of CuCl₂ and 20 mol % of 2-ethyl-2-oxazoline was added 4-phenylurazole **8**. The resulting solution was stirred at room temperature in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The solvent was removed by evaporation and the crude product was purified by flash silica gel chromatography (hexane: ethyl acetate, 1:1 v/v as the eluent).

Example procedure for the *in situ* azo-generation-Diels-Alder reaction using 4-phenylurazole with various dienes in methanol. To a methanol (20 ml) solution of cyclohexa-1,3-diene (186 mg, 2.32 mmol), CuCl₂ (16 mg, 0.12 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol) was added 4-phenylurazole (204 mg, 1.16 mmol). The resulting solution was stirred at room temperature in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The reaction was stirred for 5 h. The solvent was removed by evaporation and the crude product was purified by silica gel flash chromatography (hexane: ethyl acetate, 1:1 v/v as the eluent), giving **10a** (350 mg, 96%); mp 177-178 °C. Analytical and spectroscopic data were identical to those reported in the literature.^{35,39}

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Supplementary Material

Experimental procedures, analytical data and copies of ^1H , ^{13}C NMR spectra can be found using the link "Supplementary Material" in the journal issue contents page.

References

1. Diels, O.; Bolm, J. H.; Knoll, W. *Justus Liebigs Ann. Chem.* **1925**, 443, 242;
2. Fringuelli, F.; Taticchi, A. *The Diels-Alder Reaction: Selected Practical Methods*, Eds.; John Wiley & Sons: New York, 2002
3. Hamer, J. *1,4-Cycloaddition Reactions*, Academic Press: New York, N. Y., 1967.
4. Kawasaki, M.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, 128, 16482
<https://doi.org/10.1021/ja066726y>
5. Liu, B.; Li, K.-N.; Luo, S.-W.; Huang, J.-Z.; Pang, H.; Gong, L.-Z. *J. Am. Chem. Soc.* **2013**, 135, 3323
<https://doi.org/10.1021/ja3110472>
6. Oscarsson, K.; Oscarson, S.; Vrang, L.; Hamelink, E.; Hallberg, A.; Samuelsson, B. *Bioorg. Med. Chem.* **2003**, 11, 1235
[https://doi.org/10.1016/S0968-0896\(02\)00643-0](https://doi.org/10.1016/S0968-0896(02)00643-0)
7. Zuccarello, G.; Bouzide, A.; Kvarnström, I.; Niklasson, G.; Svensson, S. C. T.; Brisander, M.; Danielsson, H.; Nillroth, U.; Karlén, A.; Hallberg, A.; Classon, B.; Samuelsson, B. *J. Org. Chem.* **1998**, 63, 4898
<https://doi.org/10.1021/jo971562c>
8. Grange, R. L.; Gallen, M. J.; Schill, H.; Johns, J. P.; Dong, L.; Parsons, P. G.; Reddell, P. W.; Gordon, V. A.; Bernhardt, P. V.; Williams, C. M. *Chem. Eur. J.* **2010**, 16, 8894
<https://doi.org/10.1002/chem.200903454>
9. Rodgman, A.; Wright, G. F. *J. Org. Chem.* **1953**, 18, 465
<https://doi.org/10.1021/jo01133a001>
10. Tirri, T.; Aubert, M.; Pawelec, W.; Wilen, C.-E.; Pfaendner, R.; Hoppe, H.; Roth, M.; Sinkkonen J. J. *Appl. Polym. Sci.* **2014**, 131, 40413
<https://doi.org/10.1002/app.40413>
11. Pieber, B.; Martinez, S. T.; Cantillo, D.; Kappe C. O. *Angew. Chem. Int. Ed.* **2013**, 52, 10241
<https://doi.org/10.1002/anie.201303528>
12. Chaiyaveij, D.; Cleary, L.; Batsanov, A. S.; Marder, T. B.; Shea, K. J.; Whiting, A. *Org. Lett.* **2011**, 13, 3442
<https://doi.org/10.1021/ol201188d>
13. Chaiyaveij, D.; Batsanov, A. S.; Fox, M. A.; Marder, T. B.; Whiting, A. *J. Org. Chem.* **2015**, 80, 9518
<https://doi.org/10.1021/acs.joc.5b01470>
14. Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev.* **2013**, 113, 6234
<https://doi.org/10.1021/cr300527g>
15. Elwell, C. E.; Gagnon, N. L.; Neisen, B. D.; Dhar, D.; Spaeth, A. D.; Yee, G. M.; Tolman W. B. *Chem. Rev.* **2017**, 117, 2059
<https://doi.org/10.1021/acs.chemrev.6b00636>
16. Trammell, R.; Rajabimoghadam, K.; Garcia-Bosch I. *Chem. Rev.* **2019**, 119, 2954
<https://doi.org/10.1021/acs.chemrev.8b00368>

17. Lal, K.; Rani P. *ARKIVOC*, **2016**, *1*, 307
<https://doi.org/10.3998/ark.5550190.p009.593>
18. Frazier, C. P.; Engelking, J. R.; Read de Alaniz, J. *J. Am. Chem. Soc.* **2011**, *133*, 10430
<https://doi.org/10.1021/ja204603u>
19. Frazier, C. P.; Bugarin, A.; Engelking, J. R.; Read de Alaniz, J. *J. Org. Lett.* **2012**, *14*, 3620
<https://doi.org/10.1021/ol301414k>
20. Samoshin, A. V.; Hawker, C. J.; Read de Alaniz, J. *J. ACS Macro Lett.* **2014**, *3*, 753
<https://doi.org/10.1021/mz500348y>
21. Fodor, R.; Wein, J. *J. Chem. Soc.* **1948**, 684
<https://doi.org/10.1039/JR9480000684>
22. Zhu, Y.; Shi, Y. *Org. Lett.* **2013**, *15*, 1942
<https://doi.org/10.1021/ol4005917>
23. Jung, D.; Kim, M. H.; Kim J. *Org. Lett.* **2016**, *18*, 6300
<https://doi.org/10.1021/acs.orglett.6b03166>
24. Franzus, B. *J. Org. Chem.* **1963**, *28*, 2954
<https://doi.org/10.1021/jo01046a004>
25. Cohen, S. G.; Zand, R. *J. Am. Chem. Soc.* **1962**, *84*, 586
<https://doi.org/10.1021/ja00863a017>
26. Franzus, B.; Surridge, J. H. *J. Org. Chem.* **1962**, *27*, 1951
<https://doi.org/10.1021/jo01053a006>
27. Gillis, B. T.; Beck, P. E.; *J. Org. Chem.* **1962**, *27*, 1947
<https://doi.org/10.1021/jo01053a005>
28. Menard, F.; Weise, C. F.; Lautens, M. *Org. Lett.* **2007**, *9*, 5365
<https://doi.org/10.1021/ol7022054>
29. Menard, F.; Lautens, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 2085
<https://doi.org/10.1002/anie.200704708>
30. Curini M.; Epifano, F.; Marcotullio M. C.; Rosati O., *Heterocycles* **2001**, *8*, 1599
31. Kiselev, V.D.; Kornilov, D.A.; Kashaeva, E.A.; Potapova, L.N.; Konovalov, A.I. *Russ. J. Org. Chem.* **2014**, *50*, 489
<https://doi.org/10.1134/S1070428014040071>
32. Price, B.; Sutherland, I. O.; Williamson, F. G., *Tetrahedron* **1966**, *22*, 3477
[https://doi.org/10.1016/S0040-4020\(01\)92536-0](https://doi.org/10.1016/S0040-4020(01)92536-0)
33. Yi, X.; Xi, C. *Org. Lett.* **2015**, *17*, 5836
<https://doi.org/10.1021/acs.orglett.5b03009>
34. Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 6174
<https://doi.org/10.1002/anie.201001651>
35. Gillis, B. T.; Hagarty, J. D. *J. Org. Chem.* **1967**, *32*, 330
<https://doi.org/10.1021/jo01288a016>
36. Wei, Y.; Lemal, D. M. *Org. Lett.* **2004**, *6*, 3837
<https://doi.org/10.1021/ol040051r>
37. Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376
<https://doi.org/10.1021/ja00255a024>
38. Kiselev, V.D., Kornilov, D.A., Kashaeva, E.A., Potapova, L.N., Krivolapov, D.V., Litvinov, I.A., Konovalov, A.I., *Russ. J. Phys. Chem. A* **2014**, *88*, 2073

<https://doi.org/10.1134/S0036024414120152>

39. Roy, N.; Lehn, J. M. *Chem. - Asian J.* **2011**, *6*, 2419

<https://doi.org/10.1002/asia.201100244>

40. Bigelow, H. E.; Robinson, D. B *Org. Synth. Coll. Vol.* **1955**, *3*, 103.

41. Farhadi, S.; Zaringhadam, P.; Sahamieh, R. Z. *Acta Chim. Slov.* **2007**, *54*, 647

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