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Aza-Morita–Baylis–Hillman reaction of maleimides with azodicarboxylates under neat conditions

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Abstract. Green approach on reaction of diisopropylazodicarboxylate or diethyl azodicarboxylate with maleimides proceeded smoothly under neat condition at 70°C to give the corresponding hydrazine substituted pyrrolidinone as aza-Morita–Baylis–Hillman adducts in moderate to good yields in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as nitrogen Lewis base.

Keywords. Aza–Morita–Baylis–Hillman reaction; pyrrolidone; azo compound; neat reaction.

1. Introduction

The Morita–Baylis–Hillman (MBH) reaction, one of the most atom economical and important carbon–carbon bond-forming reactions,[1,2] has made great progress recently in the areas of shortening reaction time, extending the scope of the substrates, asymmetric catalysis and mechanistic studies.[3–5] For its great potential of the products for further transformation and the superior mild reaction conditions, the aza version of this reaction is extremely fascinating.[6–8] Recently, the aza-MBH reaction has received much attention[9] in which *N*-sulphonated imines (ArCH=NTs) and *N*-phosphorated imines [ArCH=NP(O)R^2] were employed as electrophiles. Reports on the usage of diisopropylazodicarboxylate (DIAD) and diethyl azodicarboxylate (DEAD) as electrophiles are scanty.[10] Over the past few years, organic reactions under solvent-free conditions have gained much popularity.[11] Solvent-free reaction conditions are not only of interest from ecological point of view, but in many cases, also offer several synthetic advantages like higher yields, reduced pollution, low cost, improved selectivities, and simplicity in process and handling.[12]

The substituted pyrrole ring system[13] is the basic building block of a number of important biological compounds including vitamin B12, chlorophyll, heme, etc.[14–16] Similarly, substituted pyrrolidinones are important components in the preparation of bile pigments,[17] and of several classes of bioactive natural compounds with a wide range of activity.[13(b),18] Figure 1 shows some of the pyrrole-based bioactive natural products.

During the course of our investigations, we found that maleimides act as activated alkenes in the MBH reaction to synthesize spirobenzofuranols.[18] In continuation of our interest in the synthesis of heterocycles[19] and the MBH reaction,[1(g),20,21] we report here aza-MBH reaction of DIAD or DEAD with maleimides in the presence of different Lewis bases and solvents.

2. Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL spectrometer at 500 MHz and 125 MHz, respectively. Mass spectra were recorded on a Thermo Finnigan LCQ Advantage MAX 6000 ESI spectrometer. Elemental analyses were recorded using a Thermo Finnigan FLASH EA 1112 CHN analyzer. Column chromatography was performed on silica gel (100–200 mesh, SRL, India). Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Merck, Germany).

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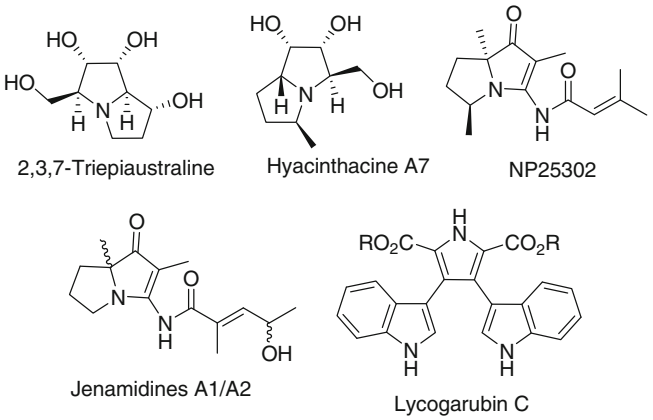


Figure 1. Natural products containing pyrrole moiety.

2.1 *Experimental procedure for the synthesis of aza-MBH adducts **3a–j***

A mixture of diisopropyl or diethyl azodicarboxylate **1a,b** (1 mmol, 1.0 equiv.), maleimides **2a–e** (1 mmol, 1.0 equiv.) and DABCO (20 mol %) was stirred at 70°C under neat condition for 2–6 h. The residue was dissolved in ethyl acetate (20 mL) and given a dil. HCl wash (1 × 20 ml) and water wash (2 × 20 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4 and removal of solvent under reduced pressure gave a crude product, which was purified by flash column chromatography with ethyl acetate: petroleum ether (20:80) as a elutent to obtain aza-MBH adducts **3a–j**.

2.1a *Diisopropyl-1-(1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3a**)*: Pale yellow; viscous liquid; IR (CH_2Cl_2): 3445, 2991, 1725, 1695, 1622, 1443, 1154 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30–1.33 (m, 12H), 2.97 (s, 3H), 4.96–5.07 (m, 2H), 6.48 (s, 1H) 7.10 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.7, 21.8, 21.9, 22.0, 23.8, 70.1, 73.1, 110.7, 141.3, 152.9, 170.0; MS m/z = 314 $[M+H]^+$; Anal. Calcd for $C_{13}H_{19}N_3O_6$ (313.13): C, 49.84; H, 6.11; N, 13.41. Found: C, 49.72; H, 6.13; N, 13.36.

2.1b *Diisopropyl-1-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3b**)*: Pale yellow; viscous liquid; IR (CH_2Cl_2): 3448, 2987, 1729, 1679, 1626, 1442, 1158 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30–1.35 (m, 12H), 4.96–5.11 (m, 2H), 6.59 (s, 1H), 7.11 (brs, 1H), 7.31 (d, 2H, J = 6.9 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.44 (t, 2H, J = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8, 21.9, 22.0, 71.0, 73.4, 111.2, 126.4, 128.1, 129.2, 131.1, 142.1, 152.6, 168.7; MS m/z = 376 $[M+H]^+$; Anal. Calcd for $C_{18}H_{21}N_3O_6$ (375.14): C, 57.59; H, 5.64; N, 11.19. Found: C, 57.81; H, 5.66; N, 11.12.

2.1c *Diisopropyl-1-(2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3c**)*: Colourless viscous liquid; IR (CH_2Cl_2): 3439, 2996, 1719, 1675, 1629, 1443, 1158 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.25–1.32 (m, 12H), 4.96–5.07 (m, 2H), 6.48 (s, 1H), 7.17 (brs, 1H), 7.67 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8, 21.9, 70.9, 73.3, 111.8, 141.9, 152.9, 169.4; MS m/z = 300 $[M+H]^+$; Anal. Calcd for $C_{12}H_{17}N_3O_6$ (299.11): C, 48.16; H, 5.73; N, 14.04. Found: C, 48.23; H, 5.68; N, 14.01.

2.1d *Diisopropyl-1-(2,5-dioxo-1-p-tolyl-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3d**)*: Yellow solid; mp 128–130°C; IR (KBr): 3442, 2997, 1728, 1685, 1621, 1448, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.24–1.32 (m, 12H), 2.34 (s, 3H), 4.95–5.07 (m, 2H), 6.62 (s, 1H), 7.15 (d, 2H, J = 8.4 Hz), 7.21 (d, 2H, J = 8.4 Hz), 7.36 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 21.7, 21.8, 21.9, 70.9, 73.2, 110.9, 126.3, 128.5, 129.8, 138.1, 141.5, 152.9, 168.9; MS m/z = 390 $[M+H]^+$; Anal. Calcd for $C_{19}H_{23}N_3O_6$ (389.16): C, 58.60; H, 5.95; N, 10.79. Found: C, 58.42; H, 5.96; N, 10.81.

2.1e *Diisopropyl-1-(1-(4-bromophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3e**)*: Colourless viscous liquid; IR (CH_2Cl_2): 3441, 2998, 1725, 1685, 1622, 1449, 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.29–1.33 (m, 12H), 4.96–5.09 (m, 2H), 6.65 (s, 1H), 7.19–7.21 (m, 2H), 7.55 (d, 2H, J = 8.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8, 21.9, 22.0, 71.0, 73.4, 111.1, 121.7, 127.7, 130.2, 132.3, 141.6, 152.9, 168.3; MS m/z = 454 $[M+H]^+$; Anal. Calcd for $C_{18}H_{20}BrN_3O_6$ (453.05): C, 47.59; H, 4.44; N, 9.25. Found: C, 47.66; H, 4.47; N, 9.39.

2.1f *Diethyl-1-(1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3f**)*: Pale yellow; viscous liquid; IR (CH_2Cl_2): 3431, 2997, 1755, 1694, 1622, 1445, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.29 (t, 3H, J = 7.6 Hz), 1.33 (t, 3H, J = 6.9 Hz), 2.97 (s, 3H), 4.21 (q, 2H, J = 6.9 Hz), 4.30 (q, 2H, J = 7.6 Hz), 6.73 (s, 1H), 7.16 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2. 14.3, 23.8, 62.9, 64.7, 110.9, 141.4, 153.4, 169.9; MS m/z = 286 $[M+H]^+$; Anal. Calcd for $C_{11}H_{15}N_3O_6$ (285.10): C, 46.32; H, 5.30; N, 14.73. Found: C, 46.19; H, 5.32; N, 14.81.

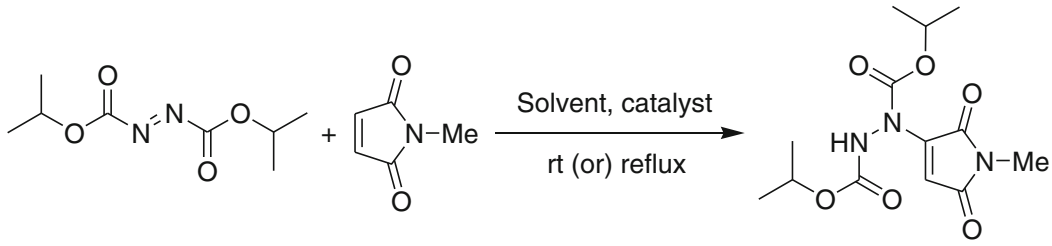
2.1g *Diethyl-1-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3g**)*: Pale yellow; viscous liquid; IR (CH_2Cl_2): 3428, 2994, 1751, 1695, 1621, 1446, 1159 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, 3H, J = 7.6 Hz), 1.34 (t, 3H, J = 7.6 Hz), 4.22 (q, 2H, J = 7.6 Hz), 4.34 (q, 2H, J = 7.6 Hz), 6.67 (s, 1H), 7.29 (d, 2H, J = 7.6 Hz), 7.34 (t, 1H, J = 7.6 Hz), 7.41–7.44 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 14.5, 62.9, 64.8, 111.3, 126.3, 128.1, 129.2, 131.1, 141.2, 153.4, 168.6; MS m/z = 348 $[M+H]^+$; Anal. Calcd for $C_{16}H_{17}N_3O_6$ (347.11): C, 55.33; H, 4.93; N, 12.10. Found: C, 55.42; H, 4.89; N, 12.19.

2.1h *Diethyl-1-(2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3h**)*: Yellow solid; mp 135–137°C; IR (KBr): 3435, 2996, 1754, 1692, 1622, 1445, 1159 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.29 (t, 3H, J = 7.6 Hz), 1.34 (t, 3H, J = 6.9 Hz), 4.23 (q, 2H, J = 6.9 Hz), 4.34 (q, 2H, J = 6.9 Hz), 6.52 (s, 1H), 7.23 (brs, 1H), 7.44 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2. 14.8, 62.7, 65.2, 110.4, 141.7, 153.6, 167.2; MS m/z = 272 $[M+H]^+$; Anal. Calcd for $C_{10}H_{13}N_3O_6$ (271.08): C, 44.28; H, 4.83; N, 15.49. Found: C, 44.37; H, 4.82; N, 15.55.

2.1i *Diethyl-1-(2,5-dioxo-1-p-tolyl-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3i**)*: Colour less solid; mp 132–134°C; IR (KBr): 3432, 2995, 1752, 1694, 1622, 1441, 1159 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, 3H, J = 7.6 Hz), 1.34 (t, 3H, J = 6.9 Hz), 2.35 (s, 3H), 4.22 (q, 2H, J = 7.6 Hz), 4.35 (q, 2H, J = 6.9 Hz), 6.65 (s, 1H), 7.16 (d, 2H, J = 8.4 Hz), 7.23 (d, 2H, J = 7.7 Hz), 7.40 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 14.5, 21.2, 62.9, 64.8, 111.3, 126.3, 128.3, 129.8, 138.2, 141.1, 153.4, 168.8; MS m/z = 362 $[M+H]^+$; Anal. Calcd for $C_{17}H_{19}N_3O_6$ (361.13): C, 56.51; H, 5.30; N, 11.63. Found: C, 56.42; H, 5.32; N, 11.54.

2.1j *Diethyl-1-(1-(4-bromophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)hydrazine-1,2-dicarboxylate (**3j**)*: Pale yellow; viscous liquid; IR (CH_2Cl_2): 3432, 2997, 1762, 1696, 1622, 1447, 1159 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (t, 3H, J = 7.6 Hz), 1.49 (t, 3H, J = 6.9 Hz), 4.12 (q, 2H, J = 7.6 Hz), 4.37 (q, 2H, J = 6.9 Hz), 6.68 (s, 1H), 7.20 (d, 2H, J = 7.6 Hz), 7.22 (brs, 1H), 7.56 (d, 2H, J = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 14.5, 63.1, 64.9, 111.3, 119.6, 124.7, 127.7, 132.3, 141.3, 151.9, 168.1; MS m/z = 426 $[M+H]^+$; Anal. Calcd for $C_{16}H_{16}BrN_3O_6$

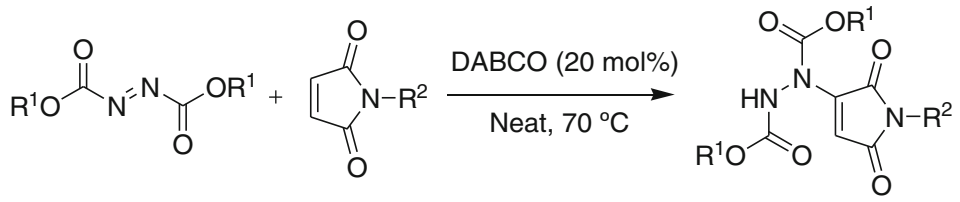
Table 1. The effects of Lewis base and solvent in the aza-MBH reaction of DIAD **1a** with *N*-methyl maleimide **2a** forming **3a**.



Entry	Solvent	Catalyst	mol %	Product	Time (h)	Yield %[a]
1	MeOH, rt	PPh_3	20	No reaction	–	–
2	MeOH, rt	DABCO	20	**3a**	10	25
3	MeOH, reflux	DABCO	20	**3a**	6	40
4	CH_2Cl_2, rt	DABCO	20	**3a**	12	28
5	THF, rt	DABCO	20	**3a**	5	50
6	DMF, rt	DABCO	20	**3a**	6	60
7	Neat, 70°C	DABCO	20	**3a**	4	85
8	Neat, 70°C	DMAP	20	**3a**	8	65
9	Neat, 70°C	Et_3N	20	**3a**	8	52
10	Neat, 70°C	DBU	20	**3a**	5	58

[a]Isolated yield after column chromatography

Table 2. Aza-MBH reaction of azodicarboxylate **1a,b** with maleimides **2a–e**.



1a,b **2a–e** **3a–j**

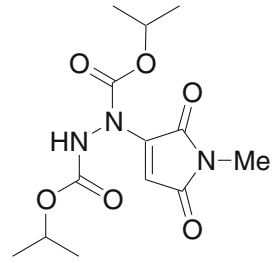
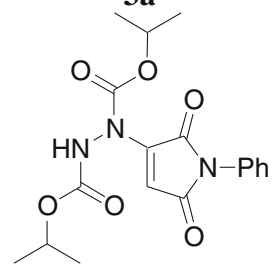
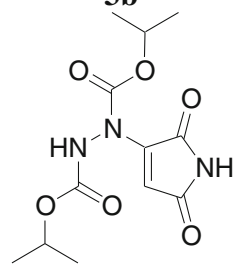
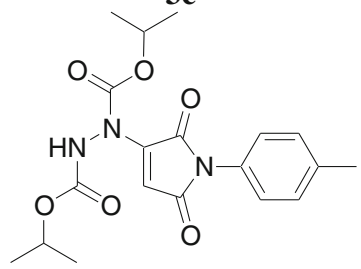
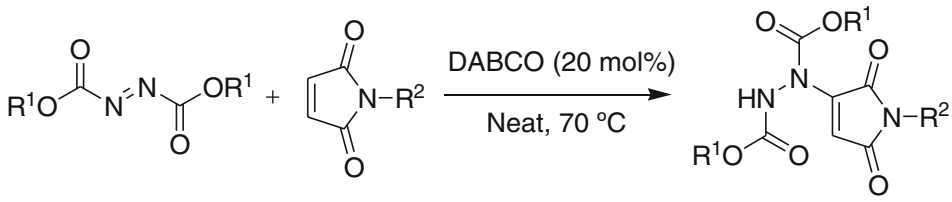
Entry	Azodicarboxylate R^1(1)		Maleimide R^2(2)		Product (3)	Time (h)	Yield (%)[a]
1	*i*Pr	**1a**	Me	**2a**	 **3a**	4.0	85
2	*i*Pr	**1a**	Ph	**2b**	 **3b**	5.0	78
3	*i*Pr	**1a**	H	**2c**	 **3c**	5.5	72
4	*i*Pr	**1a**	*p*-tolyl	**2d**	 **3d**	4.5	80

Table 2. (Continued).



1a,b **2a–e** **3a–j**

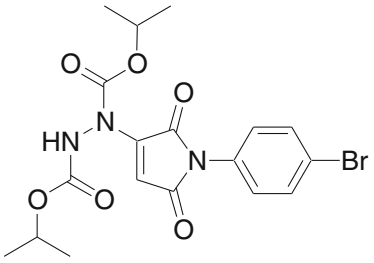
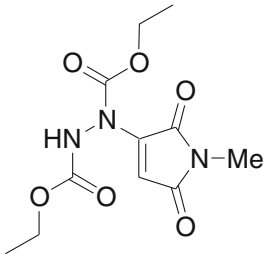
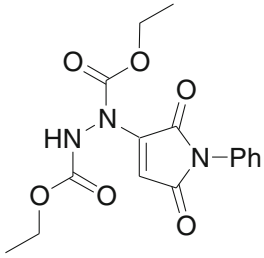
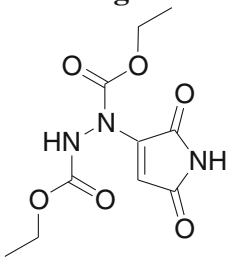
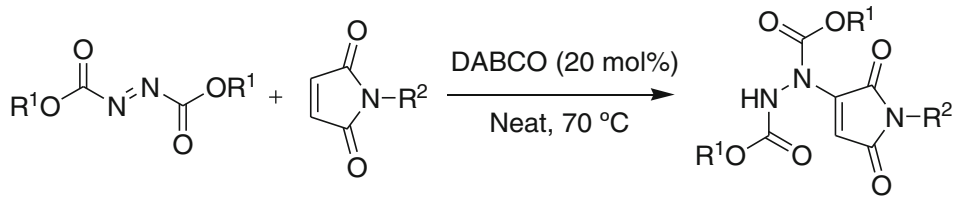
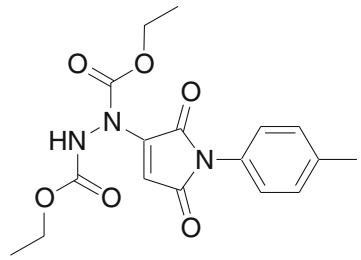
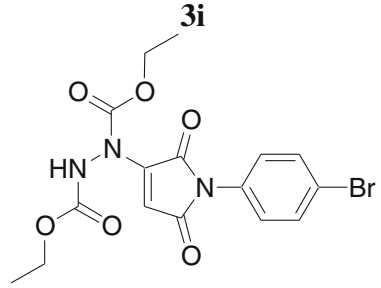
Entry	Azodicarboxylate R^1(1)		Maleimide R^2(2)		Product (3)	Time (h)	Yield (%)[a]
5	*i*Pr	**1a**	*p*-BrPh	**2e**	 **3e**	6.0	72
6	Et	**1b**	Me	**2a**	 **3f**	2.0	88
7	Et	**1b**	Ph	**2b**	 **3g**	2.5	79
8	Et	**1b**	H	**2c**	 **3h**	3	76

Table 2. (Continued).



1a,b **2a–e** **3a–j**

Entry	Azodicarboxylate R^1(1)	Maleimide R^2(2)	Product (3)	Time (h)	Yield (%)[a]
9	Et **1b**	*p*-tolyl **2d**	 **3i**	2.5	80
10	Et **1b**	*p*-BrPh **2e**	 **3j**	4.0	75

[a]Isolated yield after column chromatography

(425.02): C, 45.09; H, 3.78; N, 9.86. Found: C, 45.24; H, 3.80; N, 9.81.

3. Results and discussion

Different catalysts were first examined by carrying out the reaction of DIAD **1a** with *N*-methyl maleimide **2a** in MeOH at room temperature . The results are summarized in table 1. Phosphane Lewis base such as triphenylphosphine (PPh_3) showed no catalytic activity for this reaction (table 1, entry 1). Nitrogen Lewis base such as DABCO (20 mol%) (table 1, entry 2) could serve as an effective catalyst to give the corresponding adduct **3a**, while the yield was only 25%. Increase in temperature moderately increased the yield to 40% after 6 h (table 1, entry 3). There was no change in the yield with the increase in the catalytic amount of DABCO. Using DABCO as the catalyst, the reaction conditions were further optimized with various solvents such as CH_2Cl_2, THF, DMF at room temperature. The yield further increased to 28%, 50% and 60%, respectively (table 1, entries 4–6). On the other hand, under neat condition at 70°C the adduct **3a** was obtained in 85% yield (table 1, entry 7). Its structure was determined by spectroscopic data and elemental analysis.

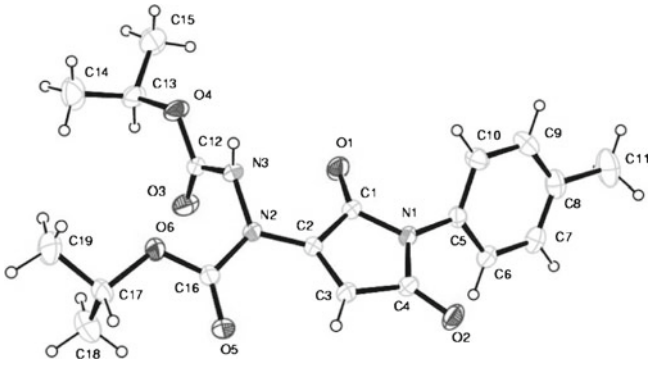


Figure 2. ORTEP diagram of compound **3d**.

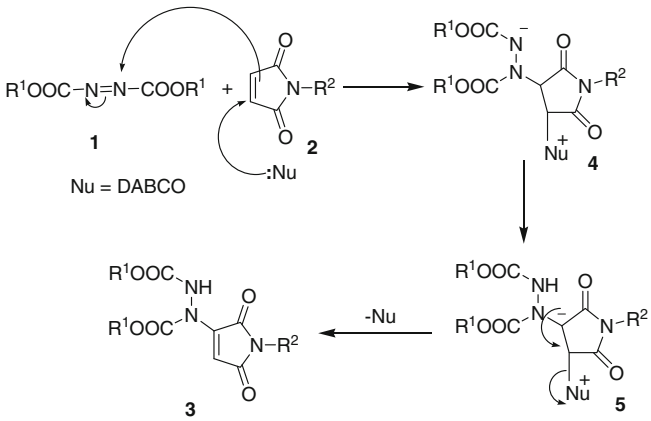


Figure 3. Plausible reaction mechanism.

In the ^{1}H NMR spectrum of compound **3a**, the three protons singlet at δ 2.97 ppm was attributed to N–CH_3 group. The two singlets at δ 6.48 and 7.10 ppm were assigned to the olefinic and $-N$H protons, respectively. The latter signal disappeared on D_2O exchange. In ^{13}C NMR spectrum, peaks at δ 152.9 and 170.0 ppm were assigned to carbamate carbonyl and amide carbons respectively. The mass spectrum revealed the molecular ion peak $[M+H]^+$ at m/z 314.

The best reaction condition for this type of aza-MBH reaction is to carry out the reaction under neat condition using DABCO as a Lewis base at 70°C. Under the optimized reaction condition the aza-MBH reaction of DIAD (**1a**) or DEAD (**1b**) with maleimides **2a–e** were examined and the corresponding aza-MBH derivatives **3a–j** were obtained in moderate to good yields. The results are summarized in table 2 (entries 1–10). Table 2 reveals the minor electronic effect of methyl, phenyl, p-Me phenyl and p-Br phenyl substituents on maleimide to the yield of the reaction. The structure was further confirmed by X-ray crystallographic analysis of the compound **3d** (figure. 2).

A tentative mechanism is described in figure 3. The reaction is believed to involve the aza-MBH reaction of **1** and **2** to form the intermediate **4** which by the abstraction of proton from the α-position of the carbonyl group forms the intermediate **5**. Subsequent elimination of the catalyst gives the aza-MBH product **3**.

4. Conclusions

In summary, we have studied the aza-MBH reaction of diisopropylazodicarboxylate and diethyl azodicarboxylate with maleimides. This reaction conditions have been optimized by varying the catalysts and solvents. Using DABCO as the catalyst under neat condition, the reaction proceeded smoothly and gave the hydrazine-substituted pyrrolidinone as adduct in good yield. Further transformation of these products is under progress.

Supplementary information

Crystallographic data for the structure **3d** in this paper have been deposited with the Cambridge Crystallographic Data centre as supplemental publication no. CCDC-779443. Copies of the data can be obtained, free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 01223 336033 or email: deposit@ccdc.cam.ac.uk).

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References

1. (a) Morita K 1968 *Japan Patent* 6 803 364; *Chem. Abstr.* 1968 **69** 58828s; (b) Morita K, Suzuki Z and Hirose H 1968 *Bull. Chem. Soc. Jpn.* **41** 2815; (c) Baylis A B and Hillman M E D 1972 *Ger. Offen.* **2** 155 113; 1972 *Chem. Abstr.* **77** 34174; (d) Hillman M E D and Baylis A B 1973 *U. S. Patent* 3 743 669; (e) Basavaiah D, Bhavani A K D, Pandiaraju S and Sarma P K S 1995 *Synlett* 243; (f) Radha Krishna P, Sachwani R and Srinivas Reddy P 2008 *Synlett* 2897; (g) Zulykama Y, Uma U, Devi P C and Perumal P T 2009 *Can. J. Chem.* **87** 1682; (h) Saikia M and Sarma J C 2010 *Can. J. Chem.* **88** 1271; (i) Shi M, Wang F-J, Zhao M X and Wei Y (eds) 2011 *The chemistry of the Morita–Baylis–Hillman reaction* (Cambridge, UK: The Royal Society of Chemistry) p 561; (j) Declerk V, Martinez J and Lamaty F 2009 *Chem. Rev.* **109** 1; (k) Gomez C, Gicquel M, Carry J-C, Schio L, Retailleau P, Voituriez A and Marinetti A 2013 *J. Org. Chem.* **78** 1488; (l) Reddy B V S, Reddy M R, Gopal Rao Y, Yadav J S and Sridhar B 2013 *Org. Lett.* **15** 464; (m) Basavaiah D, Reddy B S and Badsara S S 2010 *Chem. Rev.* **110** 5447; (n) Basavaiah D and Veeraraghavaiah G 2012 *Chem. Soc. Rev.* **41** 68
2. (a) Drewes S E and Roo G H P 1988 *Tetrahedron* **44** 4653; (b) Basavaiah D, Rao P D and Hyma R S 1996 *Tetrahedron* **52** 8001; (c) Ciganek E 1997 *Org. React.* **51** 201; (d) Langer P 2000 *Angew. Chem., Int. Ed.* **39** 3049; (e) Basavaiah D, Rao A J and Satyanarayana T 2003 *Chem. Rev.* **103** 811; (f) Ravinder M, Sadhu P S, Santhoshi A, Narender P, Swamy Gundimella Y S K, Ravikumar K and Rao J V 2010 *Synthesis* 573; (g) Wang Y, Liu L, Wang D and Chen Y-J 2012 *Can. J. Chem.* **90**(1) 85; (h) Shanmugam P and Vaithiyanathan V 2009 *Can. J. Chem.* **87**(4) 591
3. (a) Price K E, Broadwater S J, Jung H M and McQuade D T 2005 *Org. Lett.* **7** 147; (b) Aggarwal V K, Fulford

S Y and Lloyd-Jones G C 2005 *Angew. Chem., Int. Ed.* **44** 1706; (c) Price K E, Broadwater S J, Walker B J and McQuade D T 2005 *J. Org. Chem.* **70** 3980; (d) Radha Krishna P, Sachwani R and Srinivas R P 2008 *Synlett* 2897

4. (a) Santos L S, Pavam C H, Almeida W P, Coelho F and Eberlin M N 2004 *Angew. Chem., Int. Ed.* **43** 4330; (b) Krafft M E, Haxell T F N, Seibert K A and Abboud K A 2006 *J. Am. Chem. Soc.* **128** 4174; (c) Gnas Y and Glorius F 2006 *Synthesis* 1899
5. (a) Iwabuchi Y, Nakatani M, Yokoyama N and Hatakeyama S 1999 *J. Am. Chem. Soc.* **121** 10219; (b) Yang K-S, Lee W-D, Pan J-F and Chen K-M 2003 *J. Org. Chem.* **68** 915; (c) Imbriglio J E, Vasbinder M M and Miller S 2003 *J. Org. Lett.* **5** 3741; (d) McDougal N T and Schaus S E 2003 *J. Am. Chem. Soc.* **125** 12094; (e) Wang J, Li H, Yu X, Zu L and Wang W 2005 *Org. Lett.* **7** 4293; (f) Xu J, Guan Y, Yang S, Ng Y, Peh G and Tan C-H 2006 *Chem. Asian J.* **1** 724; (g) Berkessel A, Roland K and Neud€orfl J M 2006 *Org. Lett.* **8** 4195; (h) Nakano A, Takahashi K, Ishihara J and Hatakeyama S 2006 *Org. Lett.* **8** 5357
6. (a) Perlmutter P and Teo C C 1984 *Tetrahedron Lett.* **25** 5951; (b) Xu Y-M and Shi M 2004 *J. Org. Chem.* **69** 417; (c) Shi Y-L, Xu Y-M and Shi M 2004 *Adv. Synth. Catal.* **346** 1220; (d) Back T G, Rankic D A, Sorbetti J M and Wullf J E 2005 *Org. Lett.* **7** 2377; (e) Shi Y-L and Shi M 2006 *Tetrahedron* **62** 461
7. (a) Raheem I T and Jacobsen E N 2005 *Adv. Synth. Catal.* **347** 1701; (b) Buskens P, Klankermayer J and Leitner W 2005 *J. Am. Chem. Soc.* **127** 16762
8. (a) Shi M and Xu Y-M 2002 *Angew. Chem. Int. Ed.* **41** 4507; (b) Kawahara S, Nakano A, Esumi T, Iwabuchi Y and Hatakeyama S 2003 *Org. Lett.* **5** 3103; (c) Shi M, Xu Y-M and Shi Y-L 2005 *Chem. Eur. J.* **11** 1794; (d) Matsui K, Takizawa S and Sasai H 2005 *J. Am. Chem. Soc.* **127** 3680; (e) Matsui K, Tanaka K, Horii A, Takizawa S and Sasai H 2006 *Tetrahedron: Asymmetry* **17** 578; (f) Shi M and Chen L-H 2003 *Chem. Commun.* 1310; (g) Shi M, Chen L-H and Li C-Q 2005 *J. Am. Chem. Soc.* **127** 3790; (h) Shi M and Li C-Q 2005 *Tetrahedron: Asymmetry* **16** 1385; (i) Shi M, Chen L-H and Teng W-D 2005 *Adv. Synth. Catal.* **347** 1781; (j) Liu Y-H, Chen L-H and Shi M 2006 *Adv. Synth. Catal.* **348** 973; (k) Matsui K, Takizawa S and Sasai H 2006 *Synlett* 761; (l) Gausepohl R, Buskens P, Kleinen J, Bruckmann A, Lehmann C W, Klankermayer J and Leitner W 2006 *Angew. Chem., Int. Ed.* **45** 3689
9. (a) Takagi M and Yamamoto K 1991 *Tetrahedron* **47** 8869; (b) Shi M and Xu Y–M 2002 *Eur. J. Org. Chem.* 696; (c) Shi M, Xu Y–M, Zhao G–L and Wu X–F 2002 *Eur. J. Org. Chem.* 3666; (d) Shi M and Xu Y–M 2003 *J. Org. Chem.* **68** 4784; (e) Shi M and Zhao G–L 2002 *Tetrahedron Lett.* **43** 4499
10. (a) Kamimura A, Gunjigake Y, Mitsudera H and Yokoyama S 1998 *Tetrahedron Lett.* **39** 7323; (b) Shi M and Zhao G–L 2004 *Tetrahedron* **60** 2083; (c) Dadwal S, Mobin S M and Namboothiri I N N 2006 *Org. Biomol. Chem.* **4** 2525; (d) Terzidis M A, Tsiaras V G, Stephanidou-Stephanatou J, Tsoleridis C A, Psycharis V and Raptopoulou C P 2012 *Synthesis* **44** 3392
11. (a) Loh T P, Huang J M, Goh S H and Vittal J J 2000 *Org. Lett.* **29** 1291; (b) *Solvent-free organic synthesis* Tanaka K (ed) 2003 (Weinheim: Wiley-VCH); (c) Nun P, Martinez J and Lamaty F 2010 *Synthesis* 2063; (d) Roopan S M, Maiyalagan T and Khan F N 2008 *Can. J. Chem.* **86** 1019; (e) Azizi N, Mehrazma S and Saidi M R 2006 *Can. J. Chem.* **84** 800
12. (a) Cave G W W, Raston C L and Scott J L 2001 *Chem. Commun.* 2159; (b) Tanka K and Toda F 2000 *Chem. Rev.* **100** 1025; (c) Kamal A, Khan M N A, Srikanth Y V V and Reddy K S 2008 *Can. J. Chem.* **86** 1099; (d) Das S, Rahman M, Kundu D, Majee A and Hajra A 2010 *Can. J. Chem.* **88** 150
13. (a) Reddy C R, Reddy M D, Srikanth B and Prasad K R 2011 *Org. Biomol. Chem.* **9** 6027; (b) Basavaiah D, Lenin D V and Veeraraghavaiah G 2011 *Curr. Sci.* **101** 888
14. Acheson R M 1976 *An introduction to the chemistry of heterocyclic compounds* (New York: John Wiley & Sons)
15. Badger G M 1961 *The chemistry of heterocyclic compounds* (New York: Academic Press)
16. Jackson A H 1979 *Pyrroles in comprehensive organic chemistry- the synthesis and reaction of organic compounds*, Barton D and Ollis W D (eds) chapter 17.1, vol. 4 (Oxford: Pergamon Press) p 275
17. Brower J, Lightner D A and Mc Donagh A F 2001 *Tetrahedron* **57** 7813
18. (a) Marti C and Carreira E M 2005 *J. Am. Chem. Soc.* **127** 11505; (b) Duvall J R, Wu F and Snider B B 2006 *J. Org. Chem.* **71** 8579; (c) Feldman K S, Nuriye A Y and Li J 2011 *J. Org. Chem.* **76** 5042; (d) Oakdale J S and Boger D L 2010 *Org. Lett.* **12** 1132; (e) Hewlett N M and Tepe J J 2011 *Org. Lett.* **13** 4550; (f) Reddy C R, Reddy M D, Srikanth B and Prasad K R 2011 *Org. Biomol. Chem.* **9** 6027
19. (a) Karthikeyan K, Seelan T V, Lalitha K G and Perumal P T 2009 *Bioorg. Med. Chem. Lett.* **19** 3370; (b) Praveen C, Karthikeyan K, Perumal P T 2009 *Tetrahedron* **65** 9244; (c) Ramachandiran K, Karthikeyan K, Muralidharan D and Perumal P T 2010 *Tetrahedron Lett.* **51** 3006
20. Karthikeyan K and Perumal P T 2009 *Synlett* 2366
21. (a) Zulykama Y and Perumal P T 2007 *Aust. J. Chem.* **60** 205; (b) Zulykama Y and Perumal P T 2009 *Tetrahedron Lett.* **50** 3892