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REACTION OF 1-ETHOXYISOINDOLE WITH MALEIMIDE AND ITS DERIVATIVES

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Abstract – We have reported[1] the possibility of conducting the Diels-Alder [4+2]-cycloaddition reaction with isoindoles that exist predominantly in the isoindoline form, due to the Curtin-Hammet principle. Pursuing our research, we used 1-ethoxyisoindole as the most evident analog of 1-aminoisoindole. This compound is a typical simple isoindole existing chiefly as the isoindoline tautomer. We have studied the reactions of 1-ethoxyisoindoles with maleimide and its derivatives as active dienophiles. In addition, this paper describes the synthesis of a novel compound – tri-(2-methoxycarbonyl)benzylamine.

INTRODUCTION

Isoindole derivatives have found use in versatile fields: they are employed as antihypertensive,[2] antiinflamatory,[2] anorectic[3,4] agents. Some of these compounds have fungicidal properties.[5] A family of isoindole-based dyes with specific properties was created.[6-8]

Isoindole possesses interesting structural properties. The isoindole-isoindoline tautomerism is one of the key aspects in the chemistry of isoindole.[9-14] Notable is the Diels-Alder [4+2]-cycloaddition reaction,

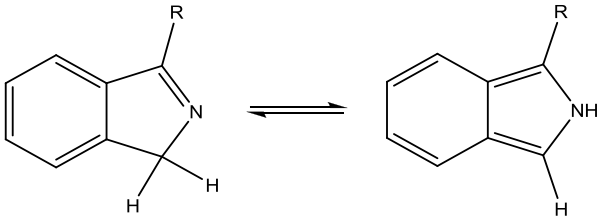
which can be used both for identification of unstable isoindoles, and to obtain unusual spatial structures, unaccessible by other methods.[15]

The cycloaddition reactions have been carried out for those isoindoles that exist predominantly in the diene form. In earlier reports[1] we have shown that though 1-aminoisoindole's most favorable tautomeic form is the isoindoline one, it can undergo Diels-Alder cycloaddition due to the Curtin–Hammett principle.

In the current publication we describe our ongoing investigation of the isoindole-isoindoline tautomerism and the possibility of reactions with dienophiles when the isoindoline form is prevalent. 2-Unsubstituted 1-ethoxyisoindole, which also exists chiefly in the isoindoline form, was chosen as a suitable analog of 1-aminoisoindole.[16] This compound is of interest because it is able to undergo condensation reactions with the formation of various fused isoindoles, and its derivatives are used to obtain anticholesterol medications.[17]

RESULTS AND DISCUSSION

The reactivity of isoindoles in [4+2]-cycloaddition reactions is generally attributed to tautomerism. For unsubstituted isoindole two tautomeric forms are relevant: the isoindoline **1a** and the isoindole **1b**. The presence of the isoindole diene tautomer in the equilibium gives us the possibility of Diels-Alder cycloaddition for isoindoles.



1a R = H
2a R = OEt

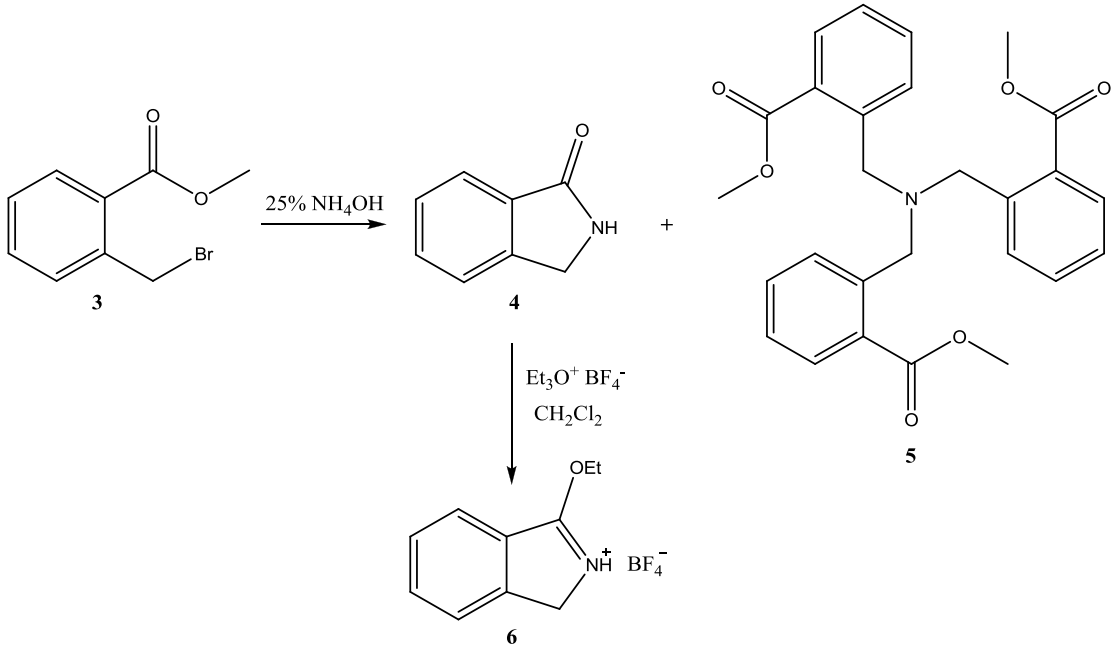
1b R = H
2b R = OEt

Scheme 1. Tautomerism of unsubstituted isoindole **1** and 1-ethoxyisoindole **2**

1-Ethoxyisoindole, in the same way as 1-aminoisoindole, exists predominantly in the isoindoline form **2a**. In contrast to unsubstituted 1-ethoxyisoindole, the 2-substituted analogs smoothly undergo cycloaddition,[18,19] as the isoindole form is their only possible tautomer. We therefore sought to use the Curtin–Hammett principle when conducting reactions of 1-ethoxyisoindoles with maleimide derivatives as dienophiles.

1-Ethoxyisoindole was obtained via alkylation of phthalimidine **4** with triethyloxonium tetrafluoroborate. Phthalimidine **4** was synthesized from the methyl ester of 2-bromomethylbenzoic acid[20] **3**.

When methyl 2-bromomethylbenzoate **3** was reacted with aqueous ammonia (25%),[20] besides the expected phthalimidine an earlier undescribed compound **5** was isolated. The reaction mixture was easily separated due to the difference in solubilities of the products in methanol. The mixture was stirred with methanol, product **5** was filtered off and the solution of phthalimidine **4** in methanol was evaporated under reduced pressure. The formation of compound **5** is explained by synchronous triple alkylation of ammonia with the 2-bromomethylbenzoic acid ester, which is not followed by a successive condensation involving the methoxycarbonyl group. The structure of compound **5** is confirmed by spectral and X-ray data.



Scheme 2. Synthesis of 1-ethoxyisoindolium tetrafluoroborate **6**

According to X-ray diffraction data the nitrogen atom in amine **5** has pyramidal configuration (sum of bond angles centered at the N(1) atom is 330.0º). Substituents adopt the propeller-like conformation. All aromatic rings are almost co-planar to the corresponding C-N(1) bond (the N(1)-C(9)-C(8)-C(7) torsion angles are -4.4(4)º for ring A, -10.4(4)º for B and -11.0(3)º for C). The benzene rings adopt antiperiplanar conformation with respect to one N(1)-C(9) bond (the C(8A)-C(9A)-N(1)-C(9C), C(8B)-C(9B)-N(1)-C(9A) and the C(8C)-C(9C)-N(1)-C(9B) torsion angles are 157.1(2)º, 161.0(2)º and 158.7(2)º, respectively) and they are almost orthogonal with respect to other N(1)-C(9) bond (the the C(8A)-C(9A)-N(1)-C(9B), C(8B)-C(9B)-N(1)-C(9C) and the C(8C)-C(9C)-N(1)-C(9A) torsion angles are -81.4(3)º, -78.3(3)º and -79.5(3)º, respectively). The orientation of the substituents at the nitrogen atom differs from the orientation of ester groups. In the case of ring A methoxy group is oriented toward the nitrogen atom (the C(8)-C(3)-C(2)-O(1) torsion angle is 14.4(4)º) while in rings B and C it has an opposite orientation (the same torsion angle is -165.3(3)º for B and -161.3(2) for C).

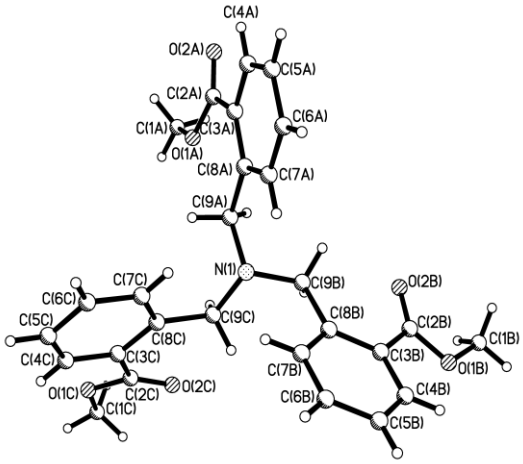
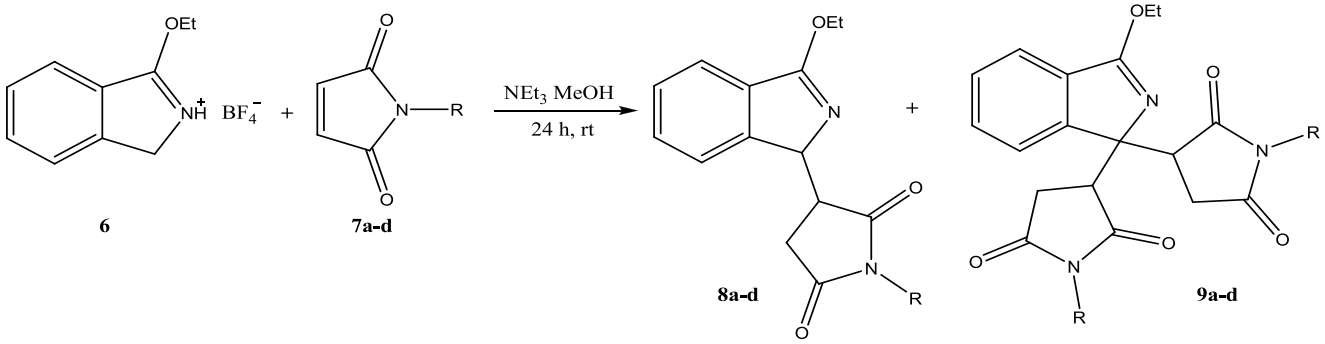


Figure 1. Structure of compound **5** according to X-ray diffraction data

1-Ethoxyisoindole tetrafluoroborate **6** obtained by a literature procedure[21] was then reacted with *N*-substituted maleimides **7a-d**. The reaction was carried out in methanol at room temperature. The free base 1-ethoxyisoindole was generated *in situ* by the addition of triethylamine. The reaction was performed using the 1:1 and 1:2 ratio of reactants.



6 **7a-d** **8a-d** **9a-d**

Maleimide	R	Ratio 1:1		Ratio 1:2	
		Yield of **8**	Yield of **9**	Yield of **8**	Yield of **9**
7a	Ph	48%	4%	53%	9%
7b	Me	-	42%	-	47%
7c	H	49%	-	51%	-
7d	*p*-C_6H_4-Me	-	44%	-	46%

Scheme 3. Interaction of 1-ethoxyisoindole with maleimides **7a–d** in the ratio 1:1 and 1:2

Eminently, regardless of the ratio of reactants, each maleimide yielded the same products in both cases. Slightly better yields of the adducts were observed for 1:2 ratio.

It is notable that by varying substituents at the maleimide nitrogen atom we can selectively obtain either *mono*- or *bis*-Michael adduct. Thus, in the case of methyl group, the final product is the *bis*-adduct. On the contrary, using unsubstituted maleimide results in *mono*-adduct as the final product. The major product at the reaction of 1-ethoxyisoindole with *N*-phenylmaleimide is the *mono*-adduct. If it is filtered off and the reaction mixture allowed to stand for some more time, a small amount of the *bis*-Michael adduct can be isolated. For tolyl group, the final product is the *bis*-adduct. The reason for the described situation is the different solubilities of **8** and **9** with different substituents: if the *mono*-adduct is soluble, it can react with the second molecule of maleimide, thus forming the *bis*-adduct which is less soluble and precipitates out.

The structure of the obtained adducts was confirmed by spectral data. The structure of *bis*-adduct **9b** was in addition confirmed by X-ray diffraction study.

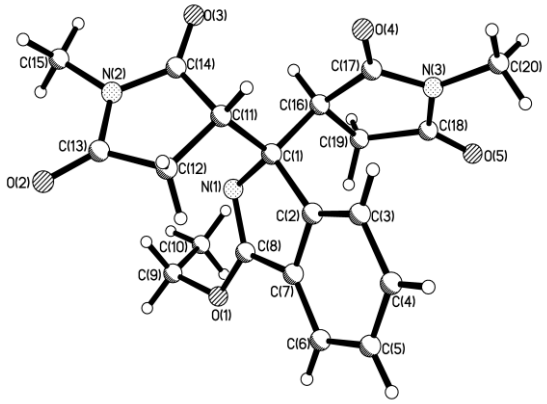
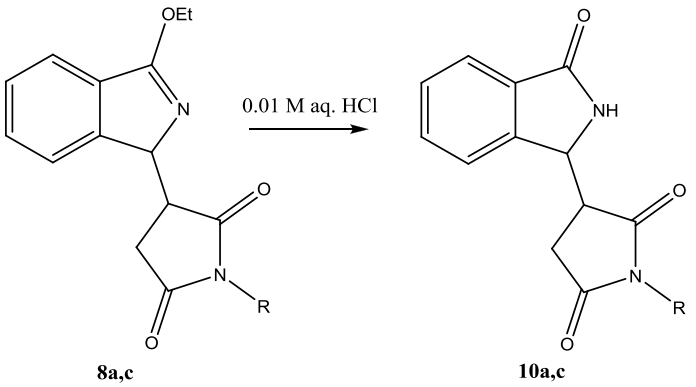


Figure 2. Structure of compound **9b** according to X-ray diffraction data

Asymmetric part of unit cell of crystals **9b** contains two molecules (A and B) differing in orientation of ethoxy group (the C(8)-O(1)-C(9)-C(10) torsion angle is 81.2º for molecule A and -94.1º for molecule B). Five-membered rings of succinimidyl fragments adopt an envelope conformation. The deviations of the C(12) and C(19) atoms from the mean plane of the remaining atoms of the ring are 0.10(2) Å and -0.10(1) Å in molecule A and 0.13(3) Å and 0.17(1) Å in B. Non-planarity of rings is promoted by steric repulsion between succinimidyl and isoindole fragments (shortened intramolecular contacts H(12A)…C(2A) 2.61 Å in molecule A, H(12D)…C(2B) 2.59 Å in molecule B (van der Waals radii sum[22] is 2.87 Å), H(12A)…C(7) 2.76 Å A and B, H(12A)…C(8) 2.74 Å A, 2.78 Å B, H(19A)…C(2) 2.77 Å A and B, H(19A)…C(8) 2.70 Å A and B, H(16A)…C(14) 2.70 Å A and B H(16A)…O(3) 2.41 Å A, 2.40 Å B (van der Waals radii sum is 2.46 Å), H(19A)…N(1) 2.58 Å A and B (van der Waals radii sum is 2.66 Å). These substituents have similar orientation with respect to the isoindole fragment (the N(1)-C(1)-C(11)-C(12) and N(1)-C(1)-C(16)-C(19) torsion angles are 57.0(6)° and -54.2(6)° in molecule

A, 57.3(6)° and -59.5(6)° in molecule B, respectively).

We successfully obtained phthalimidine derivatives of *mono*-Michael adducts with high yields. The reactions were performed in 0.01 M aqueous HCl at room temperature for 24 h, the products were collected by filtration.



Scheme 4. Hydrolysis of compound **8a,c** with the formation of phtalimidine derivatives **10a,c**

In the case of *bis*-Michael adducts no corresponding products were formed. Increasing the concentration of HCl and using elevated temperatures resulted in the degradation of the substrates due to amide bonds hydrolysis in the maleimide and phthalimidine fragments.

CONCLUSIONS

Our work presents the reaction of 1-ethoxyisoindole with maleimides. We have shown that the reactions afforded 1:1 or 1:2 adducts, depending on the substituents at the nitrogen atom in maleimide. In addition, we have proposed a procedure for the synthesis of the novel compound tri-(2-methoxycarbonyl)benzylamine. The structure of the obtained products is confirmed by spectral data and X-ray diffraction data.

EXPERIMENTAL

The NMR spectra (400.396 MHz) were recorded with a Varian Mercury 400 with TMS as internal standard. The IR-spectra were recorded on Specord M82. The chromatomass-spectra were recorded on Agilent 1100 Series with selective detector Agilent LC/MSD SL. Elemental analysis was realised with a Carlo Erba Strumenization analyser.

Procedure of the reaction of methyl ester of 2-bromomethylbenzoic acid[20] 3 with ammonia

Methyl ester of 2-bromomethylbenzoic acid[20] **3** (4.0 g, 0.017 mol) was added dropwise to the cooled

aqueous ammonia solution (25%) at 5 °C with intensive stirring. The solution was kept at room temperature for 12 h. The solvent was evaporated under reduced pressure. The residue was dissolved in water und heated to 90 °C. The oil phase was removed and charcoal was added. The mixture was heated for 1 h and the charcoal was filtered off from the hot solution. After cooling the formed precipitate was filtered. The mixture was dissolved in hot methanol and unsoluble product **5** was filtered and washed with MeOH. The filtrate was evaporated under reduced pressure with the formation of phthalimidine **4** with 78% yield (1.77 g). Spectral data for phthalimidine **4** was fully identical to the previously described in the literature.[23]

(5). 0.94 g, 12%, white solid, mp 135 °C; Anal. Calcd for $C_{27}H_{27}NO_6$: C, 70.27; H, 5.90; N, 3.03. Found: C, 70.39; H, 5.85; N, 2.78; ν_{max} (KBr) 3408, 3132, 3016, 2964, 2852, 1712, 1600, 1580, 1444, 1304, 1280, 1096, 1084, 1028, 768 cm^{-1}; δH (400 MHz, DMSOd_6) 3.78 (s, 9H), 3.89 (s, 6H), 7.29 (t, 3H), 7.49 (t, 3H), 7.71 (d, 3H); 7.73 (d, 3H); δC (100 MHz, DMSOd_6) 52.4, 55.9, 127.3, 129.8, 130.1, 130.8, 132.2, 140.0, 168.0; MS (EI): M^+, found 461. $C_{27}H_{27}NO_6$ required 461.

Common procedure for the reaction of 1-ethoxyisoindolium tetrafluoroborate[21] 6 with maleimides 7a–d

To a solution of 1-ethoxyisoindolium tetrafluoroborate **6** (0.7 g, 2.0 mmol) in MeOH (5 mL) was added the relevant maleimide **7a–d** (4.0 mmol). Triethylamine (1 mL, 7.2 mmol) was then added and the flask was sealed tightly with a stopper. After 24 h the mixture produced white plate-formed crystals. The residue was filtered and washed with MeOH. In the case of *N*-phenylmaleimide **7a** the filtrate was left for 24 h more to give compound **9a** as a precipitate.

(8a). 0.35 g, 53%, white solid, mp 177 °C; Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 70.86; H, 5.32; N, 8.46; ν_{max} (KBr) 3468, 3064, 2976, 2944, 1712, 1620, 1596, 1572, 1500, 1408, 1388, 1344, 1192, 1028, 712 cm^{-1}; δH (400 MHz, DMSOd_6) 1.25 (dd, J = 4.0, 17.6 Hz, 1H), 1.39 (t, 3H), 2.43 (dd, J = 9.2, 17.6 Hz, 1H), 3.84 (ddd, J = 3.6, 4.0, 9.2 Hz, 1H), 4.43 (q, 2H), 5.19 (d, J = 3.6 Hz, 1H), 7.25 (d, 2H), 7.42-7.57 (m, 6H), 7.73 (d, 1H); δC (100 MHz, DMSOd_6) 14.7, 28.9, 42.3, 64.4, 68.0, 120.8, 123.3, 127.5, 128.8, 129.5, 130.4, 133.1, 133.5, 151.5, 170.3, 176.0, 178.2; MS (EI): M^+, found 334. $C_{20}H_{18}N_2O_3$ required 334.

(8c). 0.26 g, 51%, white solid, mp 234 °C; Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 64.92; H, 5.34; N, 10.74; ν_{max} (KBr) 3462, 3132, 2974, 2746, 1712, 1604, 1584, 1552, 1404,

1372, 1336, 1186, 1176, 1024, 798, 752 cm^{-1}; δH (400 MHz, DMSOd_6) 1.16 (dd, *J* = 4.0, 17.6 Hz, 1H), 1.40 (t, 3H), 2.13 (dd, *J* = 9.2, 17.6 Hz, 1H), 3.62 (ddd, *J* = 3.6, 4.0, 9.2 Hz, 1H), 4.40 (q, 2H), 5.09 (d, *J* = 3.6 Hz, 1H), 7.43-7.53 (m, 3H), 7.65 (d, 1H), 11.12 (s, NH); δC (100 MHz, DMSOd_6) 14.7, 29.6, 43.3, 64.4, 67.3, 120.7, 123.1, 128.6, 130.3, 133.3, 151.9, 170.1, 178.2, 180.3; MS (EI): M^+, found 258. $C_{14}H_{14}N_2O_3$ required 258.

(9a). 0.09 g, 9%, white solid, mp 256 °C; Anal. Calcd for $C_{30}H_{25}N_3O_5$: C, 70.99; H, 4.96; N, 8.28. Found: C, 70.8.3; H, 4.83; N, 8.57; ν_{max} (KBr) 3432, 3064, 2972, 2912, 2844, 1692, 1560, 1488, 1376, 1180, 700 cm^{-1}; δH (400 MHz, DMSOd_6) 1.13 (dd, *J* = 3.2, 18.0 Hz, 1H), 1.33 (dd, *J* = 4.8, 18.0 Hz, 1H), 1.41 (t, 3H), 2.57 (dd, *J* = 8.8, 18.0 Hz, 1H), 2.70 (dd, *J* = 9.6, 18.0 Hz, 1H), 4.46 (q, 2H), 4.67 (dd, *J* = 3.2, 8.8 Hz, 1H), 4.81 (dd, *J* = 4.8, 9.6 Hz, 1H), 7.17 (d, 2H), 7.22 (d, 2H), 7.42-7.66 (m, 10H); δC (100 MHz, DMSOd_6) 14.7, 31.1, 31.4, 42.4, 42.5, 65.0, 76.2, 121.7, 122.8, 127.5, 128.9, 129.0, 129.5, 129.6, 130.2, 131.6, 132.6, 133.0, 134.7, 150.1, 170.6, 175.2, 175.5, 177.1, 177.4; MS (EI): M^+, found 507. $C_{30}H_{25}N_3O_5$ required 507.

(9b). 0.36 g, 47%, white solid, mp 227 °C; Anal. Calcd for $C_{20}H_{21}N_3O_5$: C, 62.65; H, 5.52; N, 10.96. Found: C, 62.78; H, 5.37; N, 10.74; ν_{max} (KBr) 3396, 3056, 3000, 2940, 2864, 2820, 1700, 1588, 1420, 1280, 1252, 1180, 1120, 1064, 748 cm^{-1}; δH (400 MHz, DMSOd_6) 0.93 (dd, *J* = 3.2, 18.0 Hz, 1H), 1.07 (dd, *J* = 4.8, 18.0 Hz, 1H), 1.36 (t, 3H), 2.26 (dd, *J* = 8.8, 18.0 Hz, 1H), 2.47 (dd, *J* = 9.6, 18.0 Hz, 1H), 2.85 (s, 3H), 2.88 (s, 3H), 4.35 (q, 2H), 4.54 (dd, *J* = 3.2, 8.8 Hz, 1H), 4.69 (dd, *J* = 4.8, 9.6 Hz, 1H), 7.20 (d, 1H), 7.51 (m, 2H), 7.57 (d, 1H); δC (100 MHz, DMSOd_6) 14.4, 24.7, 30.7, 30.9, 42.1, 42.2, 64.9, 75.7, 121.4, 122.4, 129.9, 131.4, 134.5, 150.1, 170.3, 176.0, 176.3, 178.0, 178.4; MS (EI): M^+, found 383. $C_{20}H_{21}N_3O_5$ required 383.

(9d). 0.49 g, 46%, white solid, mp 258 °C; Anal. Calcd for $C_{32}H_{29}N_3O_5$: C, 71.76; H, 5.46; N, 7.85. Found: C, 71.63; H, 5.37; N, 7.71; ν_{max} (KBr) 3460, 3036, 2984, 2920, 2864, 1704, 1620, 1572, 1516, 1388, 1348, 1192, 804, 776, 712 cm^{-1}; δH (400 MHz, DMSOd_6) 1.11 (dd, *J* = 3.2, 18.0 Hz, 1H), 1.31 (dd, *J* = 4.8, 18.0 Hz, 1H), 1.42 (t, 3H), 2.42 (s, 6H), 2.57 (dd, *J* = 8.8, 18.0 Hz, 1H), 2.68 (dd, *J* = 9.6, 18.0 Hz, 1H), 4.47 (q, 2H), 4.67 (dd, *J* = 3.2, 8.8 Hz, 1H), 4.82 (dd, *J* = 4.8, 9.6 Hz, 1H), 7.05 (d, 2H), 7.11 (d, 2H), 7.29 (d, 4H), 7.41 (d, 1H), 7.60 (m, 2H), 7.65 (d, 1H); δC (100 MHz, DMSOd_6) 14.7, 21.2, 31.0, 31.4, 42.4, 65.0, 76.2, 121.6, 122.8, 127.3, 129.9, 130.0, 130.2, 130.4, 131.5, 134.7, 138.4, 138.6, 150.1, 170.5, 175.3, 175.5, 177.2, 177.4; MS (EI): M^+, found 535. $C_{32}H_{29}N_3O_5$ required 535.

Common procedure for the synthesis of phtalimidine 10a,c

Compound **8a,c** (1.0 mmol) was dispersed in 10 mL of an aqueous solution of hydrogen chloride (0.01M) and kept at room temperature with vigorous stirring for 24 h. The residue was filtered and washed with water and *i*-PrOH.

(10a). 0.29 g, 96%, white solid, mp 285 °C; Anal. Calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15. Found: C, 70.67; H, 4.49; N, 8.98; ν_{max} (KBr) 3404, 3160, 3060, 2916, 2856, 1708, 1488, 1376, 1176, 756, 700 cm^{-1}; δH (400 MHz, DMSOd_6) 1.68 (dd, *J* = 4.8, 18.0 Hz, 1H), 2.23 (dd, *J* = 9.2, 18.0 Hz, 1H), 3.61 (dd, *J* = 4.8, 9.2 Hz, 1H), 5.00 (s, 1H), 7.15-7.30 (m, 6H), 7.40 (t, 1H), 7.48 (t, 2H), 8.74 (s, NH); δC (100 MHz, DMSOd_6) 28.6, 43.4, 55.4, 123.4, 123.7, 127.7, 128.8, 129.2, 132.6, 132.9, 133.1, 145.6, 170.7, 175.6, 176.9; MS (EI): M^+, found 306. $C_{18}H_{14}N_2O_3$ requires 306.

(10c). 0.22 g, 94%, white solid, mp 268 °C; Anal. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.31; H, 4.27; N, 12.03; ν_{max} (KBr) 3458, 3222, 3076, 2986, 2768, 1704, 1658, 1454, 1404, 1344, 1272, 1196, 1174, 874, 856, 774, 704 cm^{-1}; δH (400 MHz, DMSOd_6) 1.66 (dd, *J* = 4.8, 18.0 Hz, 1H), 2.22 (dd, *J* = 9.2, 18.0 Hz, 1H), 3.61 (dd, *J* = 4.8, 9.2 Hz, 1H), 5.07 (s, 1H), 7.47 (t, 1H), 7.58 (t, 1H), 7.65 (m, 2H), 8.80 (s, NH), 11.25 (s, 1H); δC (100 MHz, DMSOd_6) 29.4, 44.5, 55.1, 123.3, 123.6, 129.0, 132.5, 133.1, 145.8, 170.6, 177.9, 179.2; MS (EI): M^+, found 230. $C_{12}H_{10}N_2O_3$ required 230.

X-Ray diffraction study of compounds 5 and 9b

Crystallographic data and parameters of data collection and structure solution and refinement are listed in Table 1. Intensities of reflections were measured on an automatic «Xcalibur 3» diffractometer (graphite monochromated MoKα radiation, CCD-detector, ω scanning). Both structures were solved by direct method using SHELX97 package.[24] Positions of the hydrogen atoms were located from electron density difference maps and refined using riding model with $U_{iso}=nU_{eq}$ of carrier non-hydrogen atom (n=1.5 for methyl groups and 1.2 for other H atoms). Full-matrix least-squares refinement against F^2 within anisotropic approximation for non-hydrogen atom was performed. Final atomic coordinates, geometrical parameters and crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). CCDC dep. numbers of compounds **5** and 9**b** are 793684 and 793785, respectively.

Table 1. Crystal data and structure refinement for **5** and **9b**

Structure	**5**	**9b**
Formula	$C_{27}H_{27}NO_6$	$C_{20}H_{21}N_3O_5$
M, (g/mmol)	461.50	383.40
Unit cell dimensions, (Å, deg.)	*a*= 7.851(7), *b*= 0.011(7), *c*= 13.128(4), β= 96.58(3)	*a*= 19.366(3), *b*= 10.103(1), *c*= 21.639(4), β= 114.34(2),
Temperature, (K)	293	293
V, ($Å^3$)	4659(3)	3857.4(10)
Syngony	monoclinic	monoclinic
Space group	C2/c	P 2_1/c
Z	8	8
F, (000)	1952	1616
D_{calc}, (g/sm^3)	1.316	1.320
μ(MoK_α), (mm^{-1})	0.093	0.096
$2\theta_{max}$, (deg.)	60	50
Measured refl.	27086	8881
Independent refl.	6785	7919
R_{int}	0.170	0.128
Refl. With F>4σ(F)	2018	3934
Number of parameters	310	506
wR_2	0.097	0.143
R_1(F>4σ(F))	0.066	0.079
S	0.84	0.97
CCDC dep. Number	793684	793685

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