

Silvano Bozzini,* Patrizia Nitti, Giuliana Pitacco, Alessandro Pizzioli,
and Claudio Russo

Dipartimento di Scienze Chimiche, Università, 34127 Trieste, Italy

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Dedicated with best wishes to Professor Miha Tišler, University of Ljubljana, on the occasion of his 70th birthday.

Tricyclic compounds with an imidazolinone ring fused to 1,2- and 1,4-naphthoquinones were synthesized by a reaction of 4-amino-1,2-naphthoquinone and 2-amino-1,4-naphthoquinone with electrophilic symmetric and non symmetric diazenes.

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The interest in quinone heterocyclic derivatives is well documented in the literature [1]. In particular naphthimidazole diones and triones are prepared as dyes [2], fluorescent brighteners [3] and as compounds showing enzyme inhibition [4]. Their synthesis usually starts from 1,2- or 1,4-naphthoquinone already bearing two amino groups. Since 4-amino-1,2-naphthoquinone (**1**) and 2-amino-1,4-naphthoquinone (**2**) are easily available [5], we were induced to study their nucleophilic reactivity, with the aim of preparing quinone derivatives containing a condensed azole ring with physiological activity [6].

4-Amino-1,2-naphthoquinone (**1**) and 2-amino-1,4-naphthoquinone (**2**) are expected to behave like enamines [7]. Their ¹H and ¹³C nmr would suggest a nucleophilic reactivity for the β carbon atom of the enamine system. A comparison of the chemical shift values of their respective vinyl protons and β carbon atoms with those of the corresponding 1,2- and 1,4-naphthoquinones **3** [8] and **4** [8] is a clear indication that a considerable p-π overlapping is operating (Figure).

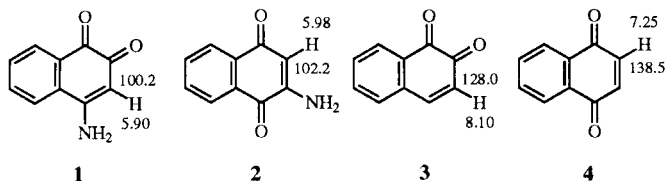


Figure. The ¹H and ¹³C nmr chemical shifts are given δ (ppm).

Actually, compounds **1** and **2**, as well as their *N*-alkyl and *N*-aryl analogs, have already been found to react with electrophiles such as methyleneiminium salts to yield salts of *C*-Mannich bases [9]. Similarly, 2-*N*-alkylamino-1,4-naphthoquinones has been found to react with dimethyl acetylenedicarboxylate in a Michael addition reaction [10].

The reactions of the substrate **2** with various alkenes under photochemical conditions leading to heterocyclic derivatives have also been explored [11]. In contrast, no

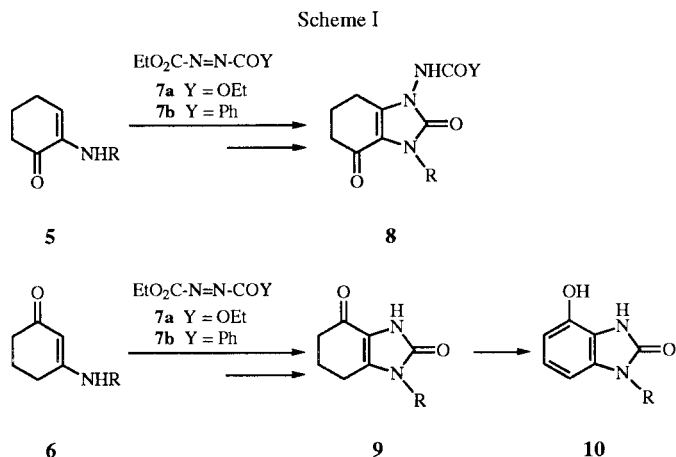
data is reported of the reaction behavior of these substrates with diazenes.

Our interest in these electrophiles arose from the fact that we have already studied their reactivity towards fully and cross-conjugated secondary enamines [12]. Both the systems **1** and **2** can be considered fully conjugated enamines and furthermore the derivative **2** is simultaneously an α-ketoenamine [7]. The α-ketoenamines **5** and the enamines **6**, the former derived from 1,2-cyclohexanedione, the latter from 1,3-cyclohexanedione react with the electrophilic diazenes **7** (Scheme I), leading eventually to the corresponding condensed imidazolinones **8** and **9**.

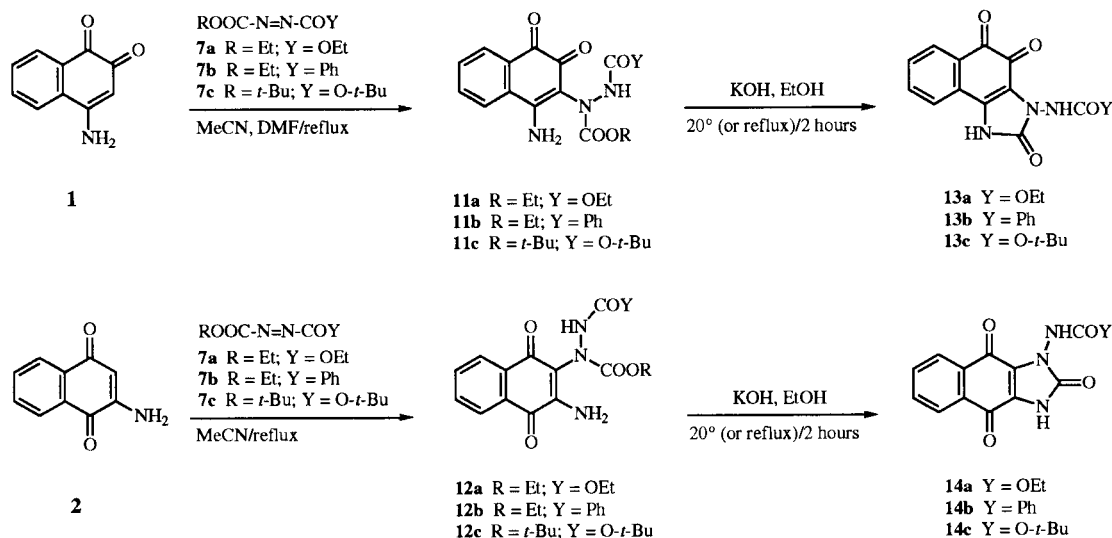
In the case of the enamines **6**, loss of the NHCOY fragment and aromatization was observed, by acidic treatment under forcing conditions, to yield eventually the benzimidazolinone derivatives **10**.

The same reagents diethylcarbonyldiazene (**7a**) and benzoylethoxycarbonyldiazene (**7b**) were chosen as electrophiles, together with di-*t*-butoxycarbonyldiazene (**7c**) (Scheme II) for the reactions with the amino naphthoquinones **1** and **2**.

The reactions were carried out in dry acetonitrile, at reflux temperature. In the reactions of the amino naphtho-



Scheme II



quinone **1**, that was partially soluble in acetonitrile, a small amount of dimethylformamide was added. The reaction times varied from 4 to 24 hours, with the exception of the reaction between compound **1** and di-*t*-butoxycarbonyldiazene (**7c**), which required at least 4 days to react partially. For the other reactions, yields were moderate to quantitative. The resulting products were the open chain hydrazino derivatives **11a-c** and **12a-c**, whose structures were established on the basis of ir, ^1H , ^{13}C nmr spectra and elemental analysis data. Some of the compounds were mixtures of conformers, as evidenced by the presence of multiple peaks for the same nucleus in the spectra (see Experimental). This can be attributed to hydrogen bonds which are able to stabilize different conformations of the hydrazino chain.

Cyclization of the adducts **11a-c** and **12a-c**, by basic treatment with potassium hydroxide in ethanol, gave the corresponding heterocyclic quinones **13a-c** and **14a-c**, with loss of ethanol or *t*-butyl alcohol. Prolonged heating was used only for the *t*-butylated compounds **11c** and **12c**, thus demonstrating that the cyclization reaction is subject to steric limitations.

The structures of the quinone imidazolinones have been determined by means of spectroscopic data. A naphth[2,3*d*]-imidazole-2,4,9-trione similar to **14a-c** has been prepared by Kallmayer and Binger [13] by treatment of 2-arylamino-3-trichloroacetyl-amino-1,4-naphthoquinones with a basic solution. As to the problem of a possible presence of hydroxyimidazole tautomers for the derivatives **13** and **14**, this was excluded for most of the compounds, on the basis of lack of absorption bands between 3600 and 3400 cm^{-1} , as suggested for analogous derivatives [13]. Only compound **14b** showed multiple bands within this range. Like the hydrazino compounds **11a-c** and **12a-c**, also the imidazolinones **13a-c** and **14a-c** were characterized by the presence of multiple bands

both in the ir and nmr spectra, in the solid state and in solution, which would account for the existence of strong hydrogen bonds (intermolecular and intramolecular).

EXPERIMENTAL

Melting points were determined with a Büchi apparatus and are uncorrected. The ir spectra were recorded in nujol mulls, unless otherwise stated, on a Perkin Elmer 1320 spectrometer. The ^1H and ^{13}C nmr spectra were scanned on a JEOL EX400 (400 MHz for proton and 100.4 MHz for carbon) using either deuteriochloroform or mixtures deuteriochloroform-dimethyl sulfoxide- d_6 (few drops) as solvent and tetramethylsilane as internal standard. *J* values are given in Hz. Analysis (tlc) were performed on Merck silica gel 60 F₂₅₄ plates. Flash chromatography was run on Merck silica gel 230-400 mesh ASTM (Kieselgel 60, Merck). Light petroleum refers to the fraction with bp 40-70° and ether to diethyl ether. Analytical values reported for compounds **11b**, **13a**, and **14b** are the best available after repeated elemental analyses.

Synthesis of the Reactants.

4-Amino-1,2-naphthoquinone (**1**) and 2-amino-1,4-naphthoquinone (**2**) were prepared as reported in reference [5], diethoxycarbonyldiazene (**7a**) and di-*t*-butoxycarbonyldiazene (**7c**) were purchased from Aldrich, benzoylethoxycarbonyldiazene (**7b**) was prepared following the method reported in reference [14].

General Procedure for the Reaction of Aminonaphthoquinones **1** and **2** with Diazenes **7**.

A solution of 4-amino-1,2-naphthoquinone (**1**) and the diazenes **7** in excess was heated in a 1:1 mixture of acetonitrile and dimethylformamide, while the reactions between 2-amino-1,4-naphthoquinone (**2**) was heated in refluxing acetonitrile. The solvent was removed and the product was crystallized. When the reaction was not complete, the product was purified by flash chromatography. The cyclization reactions were carried out in

ethanolic potassium hydroxide. Water was added and the solutions were acidified with 5% hydrochloric acid and extracted with dichloromethane. After the usual workup the product was either crystallized or purified on column chromatography.

4-Amino-1,2-Naphthoquinone (**1**) [5]

ir: ν NH 3400, 3320, 3190, 1520, ν C-H 3060, ν CO 1695, ν C=C and Ar 1645, 1600, 1585, 1565 cm^{-1} ; ^1H nmr: δ 8.25 (br s, 2H, NH_2), 8.03 (dt, 2H, 5-H, 8-H), 7.74 (dt, 1H, 6-H or 7-H, $J = 7.8, 1.4$ Hz), 7.64 (dt, 1H, 6-H or 7-H, $J = 7.8, 1.4$ Hz), 5.90 (s, 1H, vinyl-H); ^{13}C nmr: δ 181.3 (s), 173.8 (s), 157.4 (s), 132.9 (d), 130.6 (s), 130.3 (d), 129.6 (s), 126.7 (d), 123.0 (d), 100.2 (d).

2-Amino-1,4-Naphthoquinone **2** [5].

ir: ν NH 3372, 3318, 3289, 3224, 3183, ν C-H 3064, ν CO 1685, ν C=C and Ar 1633, 1614, 1594, 1558 cm^{-1} ; ^1H nmr: δ 7.98 (2 dd, $J_1 = 7.8$ Hz, $J_2 = 1.4$ Hz, 2H, 5-H, 8-H), 7.72 (dt, 1H, 6-H or 7-H, $J = 7.8, 1.4$ Hz), 7.63 (dt, 1H, 6-H or 7-H, $J = 7.8, 1.4$ Hz), 6.66 (br s, 2H, NH_2), 5.98 (s, 1H, vinyl-H); ^{13}C nmr: δ 182.1 (s), 181.0 (s), 148.9 (s), 133.3 (d), 132.4 (s), 130.8 (d), 129.5 (s), 124.9 (d), 124.5 (d), 102.2 (d).

3-(*N,N'*-Diethoxycarbonyl)hydrazino-4-amino-1,2-naphthoquinone (**11a**).

The reaction of **1** (0.17 g, 1 mmole) with diethoxycarbonyldiazene (**7a**) (0.17 g, 1 mmole) according to the general procedure for 4 hours gave 0.25 g (75%) of **11a**, mp 230°, from ethanol; ir: ν NH 3390, 3340, 3320, 3220, 1520, ν CO 1725, 1720, 1695, 1650, ν C=C and Ar 1600, 1580, 1580, 1490, 790, 760, 730 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 8.86 (br s, 1H, NH), 8.37 (br s, 2H, NH_2), 7.99 (m, 2H, aromatic protons), 7.64 (t, 1H, aromatic protons), 7.54 (t, 1H, aromatic protons), 4.08 (m, 4H, 2 CH_2), 1.19 (t, 4.2H, CH_3), 1.10 (br t, 1.8H, CH_3); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 181.9 (2 s), 158.9 (s), 155.5 (s), 134.3 (d), 131.8 (d), 131.3 (s), 129.1 (s), 128.3 (d), 124.9 (d), 62.8 (t), 62.0 (t), 14.3 (q), 14.2 (q).

Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6$ ($M = 347.33$): C, 55.33; H, 4.93; N, 12.10. Found C, 55.41; H, 4.78; N, 11.80.

3-(*N*-Benzoyl-*N'*-ethoxycarbonyl)hydrazino-4-amino-1,2-naphthoquinone (**11b**).

The reaction of **1** (0.17 g, 1 mmole) with benzoylethoxycarbonyldiazene (**7b**) (0.20 g, 1 mmole) according to the general procedure for 3 hours gave 0.32 g (86%) of **11b**, mp 225-226°, from chloroform-light petroleum; ir: ν NH 3380, 3310, 3190, 1510, ν CO 1740, 1710, 1690 (C=O, CO_2Et), ν C=C and Ar 1615, 1605, 1585 cm^{-1} ; ^1H nmr: δ 10.70 (s, 1H, NHCO), 8.91, 8.50 (2 br s, 2H, NH_2), 8.04 (m, 2H, aromatic protons), 7.90 (m, 2H, aromatic protons), 7.66-7.10 (m, 5H, aromatic protons), 4.12 (m, 2H, CH_2CH_3), 1.24, 1.20, 1.12 (3 t, 3H, CH_2CH_3); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 181.3 (2 s), 169.8 (s), 168.5 (s), 155.0 (s), 133.7 (d), 131.5 (d), 131.1 (d), 130.1 (s), 128.6 (s), 127.6 (d), 127.5 (d), 127.3 (d), 127.2 (s), 124.4 (d), 115.0 (s), 62.0 (t), 39.2 (q).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_5$ ($M = 379.37$): C, 63.32; H, 4.52; N, 11.08. Found C, 62.80; H, 4.34; N, 10.82.

3-(*N,N'*-Di-*t*-butoxycarbonyl)hydrazino-4-amino-1,2-naphthoquinone (**11c**).

The reaction of **1** (0.17 g, 1 mmole) with di-*t*-butoxycarbonyldiazene (**7c**) (0.23 g, 1 mmole) according to the general

procedure for 4 days gave 0.10 g (25%) of **11c**, mp 190° dec; ir: ν NH 3400, 3320, 3180, 1520, ν CO 1725, 1700, 1660, ν C=C and Ar 1605, 1580 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 10.83 (s, 1H, NH), 9.37, 9.09, 8.83, 8.70 (4 br s, 2H, NH_2), 8.10 (m, 2H, aromatic protons), 7.75 (m, 2H, aromatic protons), 1.45, 1.42, 1.41, 1.38 (3 s, 9H, *t*-Bu); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 181.4 (2 s), 169.9 (s), 168.5 (s), 155.7 (d), 155.0 (d), 133.8 (d), 131.6 (d), 131.3 (d), 130.7 (2 s), 128.5 (d), 127.7 (2 d), 127.2 (d), 126.9 (s), 124.4 (d), 62.2 (t), 13.7 (q).

Anal. Calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_6$ ($M = 403.44$): C, 59.54; H, 6.25; N, 10.42. Found C, 59.38; H, 6.10; N, 10.13.

2-(*N,N'*-Diethoxycarbonyl)hydrazino-3-amino-1,4-naphthoquinone (**12a**).

The reaction of **2** (0.17 g, 1 mmole) with diethoxycarbonyldiazene (**7a**) (0.17 g, 1 mmole) according to the general procedure for 46 hours gave 0.20 g (59%) of **12a**, mp 165-166°, from ethanol; ir: ν NH 3400, 3260, ν CO 1725, 1690, ν C=C and Ar 1610, 1575 cm^{-1} ; ^1H nmr: δ 10.2 (br s, 1H, NH), 8.09 (m, 2H, 5-H, 8-H), 7.74, 7.64 (2 br t, 2H, 6-H, 7-H), 7.37 (br s, 2H, NH_2), 4.24 (m, 4H, CH_2CH_3), 1.29, 1.20, 1.18 (3 t, 6H, CH_2CH_3); ^{13}C nmr, δ 181.8 (s), 178.4 (s), 158.5 (s), 156.0 (s), 146.5 (s), 135.0 (d), 132.5 (d), 130.5 (2 s), 126.5 (d), 126.4 (d), 117.2 (s), 63.4 (t), 62.7 (t), 14.3 (2 q).

Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6$ ($M = 347.33$): C, 55.33; H, 4.93; N, 12.10. Found C, 55.65; H, 5.11; N, 12.48.

2-(*N*-Benzoyl-*N'*-ethoxycarbonyl)hydrazino-3-amino-1,4-naphthoquinone (**12b**).

The reaction of **2** (0.17 g, 1 mmole) with benzoylethoxycarbonyldiazene (**7b**) (0.26 g, 1 mmole) according to the general procedure for 4 hours gave 0.41 g (95%) of **12b**, mp 170°, from ethanol-water; ir: ν NH 3440, 3380, 3260, 3220, 1520, ν CO 1740, 1720, 1705, 1680, 1665, ν Ar 1615, 1595, 1570 cm^{-1} ; ^1H nmr: δ 8.91 (br s, 1H, NH), 8.06 (m, 2H, 5-H, 8-H), 7.8-7.4 (m, 8H, NH, 6-H, 7-H, C_6H_5), 6.0 (2 br s, 1H, NH), 4.21 (m, 2H, CH_2), 1.21, 1.19 (2 t, 3H, CH_3); ^{13}C nmr: δ 181.6 (s), 181.5 (s), 178.6 (s), 179.0 (s), 169.1 (s), 168.3 (s), 155.5 (s), 154.5 (s), 147.5 (s), 147.2 (s), 134.9 (d), 132.5 (d), 132.4 (d), 131.5 (s), 130.5 (s), 128.7 (d), 127.5 (d), 126.5 (d), 126.4 (d), 116.8 (s), 116.3 (s), 63.3 (t), 14.3 (q).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_5$ ($M = 379.37$): C, 63.32; H, 4.52; N, 11.08. Found: C, 63.75; H, 4.60; N, 11.20.

2-(*N,N'*-Di-*t*-butoxycarbonyl)hydrazino-3-amino-1,4-naphthoquinone (**12c**).

The reaction of **2** (0.17 g, 1 mmole) with di-*t*-butoxycarbonyldiazene (**7c**) (0.23 g, 1 mmole) according to the general procedure for 4 hours gave 0.15 g (37%) of **12c**, mp 208-209°, from ethanol; ir: ν NH 3410, 3220, ν CO 1725, 1705, 1680, ν C=C, Ar 1640, 1620, 1590, 1580 cm^{-1} ; ^1H nmr: δ 8.08 (m, 2H, 5-H, 8-H), 7.72 (m, 1H, 6-H or 7-H), 7.64 (m, 1H, 6-H or 7-H), 7.35, 7.20, 7.03, 6.99, 5.80 (5 br s, 3H, NH, NH_2), 1.52, 1.48, 1.38 (3 s, 18H, *t*-Bu); ^{13}C nmr: δ 181.3 (s), 181.2 (s), 177.6 (s), 177.3 (s), 157.0 (s), 156.7 (s), 153.9 (s), 146.6 (s), 145.7 (s), 134.2 (d), 131.8 (s), 131.6 (d), 129.8 (s), 125.6 (d), 125.5 (d), 117.2 (s), 116.1 (s), 116.0 (s), 81.4, 81.3, 80.9 (3 s), 27.5, 27.4, 27.3 (3 q).

Anal. Calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_6$ ($M = 403.44$): C, 59.54; H, 6.25; N, 10.42. Found C, 60.20; H, 5.78; N, 10.11.

3-Ethoxycarbonylamino-2,3,4,5-tetrahydro-1*H*-naphth[1,2-*d*]-imidazole-2,4,5-trione (**13a**).

According to the general procedure, basic treatment of compound **11a** (0.15 g, 0.4 mmole) for 24 hours at room temperature furnished **12a** (0.10 g, 85%), mp 260°, from absolute ethanol; ir: ν NH 3430, 3380, 3350, 3270, ν CO 1730, 1710, 1660, ν C=C and Ar 1640, 1585, 1490 cm^{-1} ; ^1H nmr: δ 12.3 (br s, 1H, NH), 9.20 (s, 1H, NH), 7.97 (d, 1H, 6-H), 7.73 (d, 1H, H-9), 7.62 (t, 1H, 8-H), 7.45 (t, 1H, 7-H), 4.23 (bm, 2H CH_2), 1.33 (t, 3H, CH_3), ^{13}C nmr: δ 179.4 (s), 164.4 (s), 155.3 (s), 151.4 (s), 135.0 (s), 134.7 (d), 129.7 (d), 129.3 (d), 128.9 (s), 125.9 (s), 123.1 (d), 118.5 (s), 61.5 (t), 13.9 (q).

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_5$ ($M = 301.26$): C, 55.82; H, 3.68; N, 13.95. Found C, 55.18; H, 3.73; N, 13.60.

3-Benzoylamino-2,3,4,5-tetrahydro-1*H*-naphth[1,2-*d*]imidazole-2,4,5-trione (**13b**).

According to the general procedure, basic treatment of compound **11b** (0.20 g, 0.5 mmole) for 24 hours at room temperature furnished compound **13b** (0.04 g, 20%), mp 289-291° dec, from dichloromethane-light petroleum; ir: ν NH 3360, 1505, ν CO 1720, 1690, 1650, ν C=C and Ar 1620, 1600, 1580 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 811.85 (s, 1H, NH), 8.80 (b s, 1H, NH), 7.80 (m, 9H, aromatic protons); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 179.0 (s), 163.5 (s), 154.7 (s), 152.2 (s), 135.3 (s), 135.2 (d), 132.2 (d), 131.8 (s), 130.3 (d), 130.0 (d), 129.1 (s), 128.4 (d), 128.2 (d), 126.7 (s), 123.6 (d), 118.4 (s).

Anal. Calcd. for $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_4$ ($M = 333.30$): C, 64.87; R 3.33; N, 12.61. Found: C, 65.15; H, 3.45; N, 12.74.

3-*t*-Butoxycarbonylamino-2,3,4,5-tetrahydro-1*H*-naphth[1,2-*d*]imidazole-2,4,5-trione (**13c**).

According to the general procedure, basic treatment of compound **11c** (0.15 g, 0.4 mmole) under reflux for 30 minutes furnished **13c** (0.02 g, 15%), mp 290° dec, from dichloromethane-light petroleum; ir: ν NH 3330, 3300, 3100, 1510, ν CO 1730, 1705, 1665, ν C=C and Ar 1635, 1630, 1615, 1585, 1490 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 9.00 (br s, 1H, NH), 7.91 (d, 1H, 6-H), 7.65 (d, 1H, H-9), 7.53 (t, 1H, 8-H), 7.40 (s, 1H, NH), 7.37 (t, 1H, 7-H), 1.44 (s, 9H, *t*-Bu); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 179.6 (s), 164.7 (s), 154.3 (s), 151.7 (s), 135.1 (s), 134.8 (d), 129.8 (d), 129.5 (d), 129.1 (s), 126.2 (s), 123.1 (d), 118.7 (s), 81.5 (s), 27.8 (q).

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_5$ ($M = 329.31$): C, 58.36; H, 4.59; N, 12.76. Found C, 58.75; H, 4.65; N, 12.51.

1-Ethoxycarbonylamino-2,3,4,9-tetrahydro-1*H*-naphth[2,3-*d*]imidazole-2,4,9-trione (**14a**).

According to the general procedure, basic treatment of compound **12a** (0.20 g, 0.6 mmole) under reflux for 24 hours furnished **14a** (0.16 g, 95%), mp 230° dec, from dichloromethane-light petroleum; ir: ν NH 3320, 3240, ν CO 1740, 1730, 1665, ν Ar 1615, 1590 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 10.2, 9.85, 8.47 (3 br s, 2H, NH), 8.01 (m, 2H, 5-H, 8-H), 7.72 (m, 2H, 6-H, 7-H), 4.50, 4.25, 4.13 (3 bq, 2H, CH_2), 1.35, 91.24, 1.13 (3 t, 3H, CH_3); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 173.6 (s), 172.4 (s), 154.8 (s), 150.8 (s), 132.8 (d), 132.5 (d), 130.8 (s), 130.0 (s), 125.1 (d), 125.0 (d), 124.6 (s), 124.0 (s), 61.1 (t), 13.6 (q).

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_5$ ($M = 301.26$): C, 55.82; H, 3.68; N, 13.95. Found C, 55.50; H, 3.65; N, 13.60.

1-Benzoylamino-2,3,4,9-tetrahydro-1*H*-naphth[2,3-*d*]imidazole-2,4,9-trione (**14b**).

According to the general procedure, basic treatment of **12b** (0.25 g, 0.7 mmole) for 24 hours at room temperature gave **14b** (0.21 g, 95%), which was purified by flash chromatography (eluant: light petroleum:ethyl acetate 2:1), mp 295° dec, from ethanol; ir: ν NH 3420, 3320, 3240, 3180, 1520, ν CO 1730, 1665, ν Ar 1610, 1590, 1580 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 11.35 (s, 1H, NH), 8.04 (m, 5H, C_6H_5), 7.77 (m, 2H, 5-H, 8-H), 7.64 (m, 1H, 6-H or 7-H), 7.56 (m, 2H, 6-H or 7-H, NH); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 174.0 (s), 172.8 (s), 166.4 (s), 151.1 (s), 133.0 (d), 132.8 (d), 131.7 (d), 131.2 (s), 131.0 (s), 130.5 (s), 127.8 (d), 127.5 (d), 125.4 (d), 125.3 (d), 125.2 (s), 124.8 (s).

Anal. Calcd. for $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_4$ ($M = 333.30$): C, 64.87; H, 3.33; N, 12.61. Found: C, 64.80; H, 3.29; N, 12.10.

1-*t*-Butoxycarbonylamino-2,3,4,9-tetrahydro-1*H*-naphth[2,3-*d*]imidazole-2,4,9-trione (**14c**).

According to the general procedure, basic treatment of **12c** (0.15 g, 0.4 mmole) under reflux for 30 minutes gave **14c** (0.03 g, 25%), which was purified by flash chromatography (eluant: light petroleum:ethyl acetate 2:1), mp 200°; ir: ν NH 3350, ν CO 1755, 1720, 1660, ν Ar 1615, 1595 cm^{-1} ; ^1H nmr (deuteriochloroform + DMSO- d_6): δ 11.75 (br s, 1H, NH), 9.0 (b s, 1H, NH), 7.87 (m, 2 H, 5-H, 8-H), 7.53 (m, 2H, 6-H, 7-H), 1.49, 1.38, 1.09 (3 s, 9H, *t*-Bu); ^{13}C nmr (deuteriochloroform + DMSO- d_6): δ 172.5 (s), 171.2 (s), 152.3 (s), 149.6 (s), 131.7 (d), 131.3 (d), 130.9 (s), 130.4 (s), 125.9 (d), 125.7 (d), 124.8 (s), 124.4 (s), 81.5 (s), 27.6 (q).

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_5$ ($M = 329.31$): C, 58.36; H, 4.59; N, 12.76. Found C, 58.68; H, 4.67; N, 12.64.

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