Synthesis of new stable crystalline zwitterionic products from the reactions of 1-methylimidazole, acetylenic esters and strong cyclic CH-acids

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The reactive 1:1 intermediate produced in the reaction between 1-methyl imidazole and dialkyl acetylenedicarboxylates was trapped by strong cyclic CH-acids such as *N,N′*-dimethylbarbituric acid, Meldrum's acid, cyclohexan-1, 3-dione, indan-1,3-dione, cyclopentan-1,3-dione and tetronic acid to yield stable 1,4-diionic imidazolium betaines in excellent yields.

Keywords: dialkyl acetylenedicarboxylate, 1-methylimidazole, nitrogen betaines, CH-acids, Zwitterionic species

Zwitterionic species often result from the addition of nucleophiles to activated alkynes like dimethyl acetylenedicarboxylate (DMAD).[1] A variety of nucleophiles such as triphenyl phosphine,[2] tertiary amines,[3] dimethyl sulfoxide,[4] nitrogen-containing heterocycles,[5] *etc*. has been known to generate active zwitterionic species by this pathway.

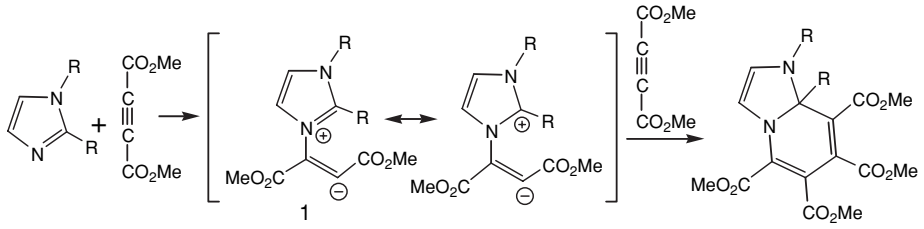
The reaction of *N*-heterocycles with DMAD, generally involves the initial addition of the *N*-heterocycle to DMAD to form a dipolar intermediate, *e.g.* **1**, which undergoes further reaction with DMAD leading to a variety of complex heterocyclic compounds; such reactions have been the subject of detailed investigations by several research groups.[5-10] For example, simple imidazoles are transformed into imidazo[1,2-*a*]pyridines on treatment with DMAD in ether at room temperature (Scheme 1).[10]

Furthermore, these highly reactive intermediates can be captured by suitable substrates such as carbon dioxide,[11] isocyanates,[12] dialkyl azodicarboxylates,[12] carbonyl compounds,[13] *N*-tosylimines,[13d,14] arylmethylidenemalononitriles[15] and CH-acids.[16] As early as 1965, Bamfiled and his co-workers showed that pyridine reacts smoothly with DMAD in the presence of dimethyl malonate as a CH-acid to form cyclohepta-1,3-diene derivatives.[16]

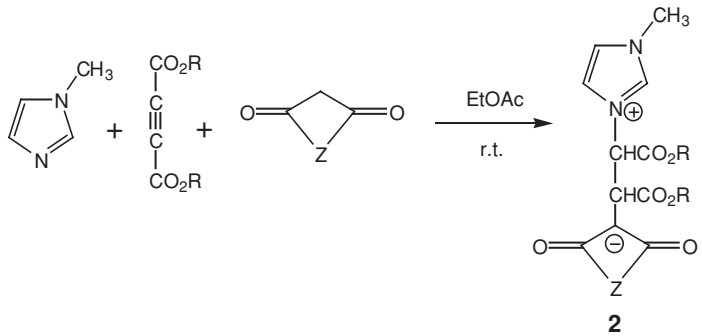
In view of our general interest in multi-component reactions involving zwitterionic species,[17] we examined the reaction of 1-methylimidazole with acetylenic esters and strong cyclic CH-acids as trapping agents for the reactive dipole intermediate. Thus, reaction of dialkyl acetylenedicarboxylates with 1-methylimidazole in the presence of strong cyclic CH-acids such as *N,N′*-dimethylbarbituric acid, Meldrum's acid, cyclohexan-1,3-dione, indan-1,3-dione, cyclopentan-1,3-dione and tetronic acid leads to the corresponding stable 1,4-diionic imidazolium betaines **2** in excellent yields (Scheme 2).

The two cyclic five and seven-membered rings structures for compound **2** are unlikely because they require several and different chemical shift coincidences in the ^{1}H and ^{13}C NMR spectra. Interestingly, it has been found that this reaction is highly chemoselective in the preparation of betaine **2**, since neither cyclic products **5** or **6** were detected.

Although the mechanism of this reaction has not been established in an experimental manner, but a mechanistic rationalisation is provided in **Scheme 3**. The initial addition of 1-methylimidazole to dialkyl acetylenedicarboxylate and



Scheme 1



2	R	Z	Yield (%)
a	CH_3	CH_3N-CO-NCH_3	97
b	CH_3	O-$C(CH_3)_2$-O	95
c	CH_3	CH_2-CH_2-CH_2	74
d	CH_3	*ortho*-C_6H_4	96
e	CH_3	CH_2-CH_2	71
f	CH_3	CH_2-O	82
g	CH_2CH_3	CH_3N-CO-NCH_3	92
h	CH_2CH_3	O-$C(CH_3)_2$-O	93
i	CH_2CH_3	*ortho*-C_6H_4	90

Scheme 2

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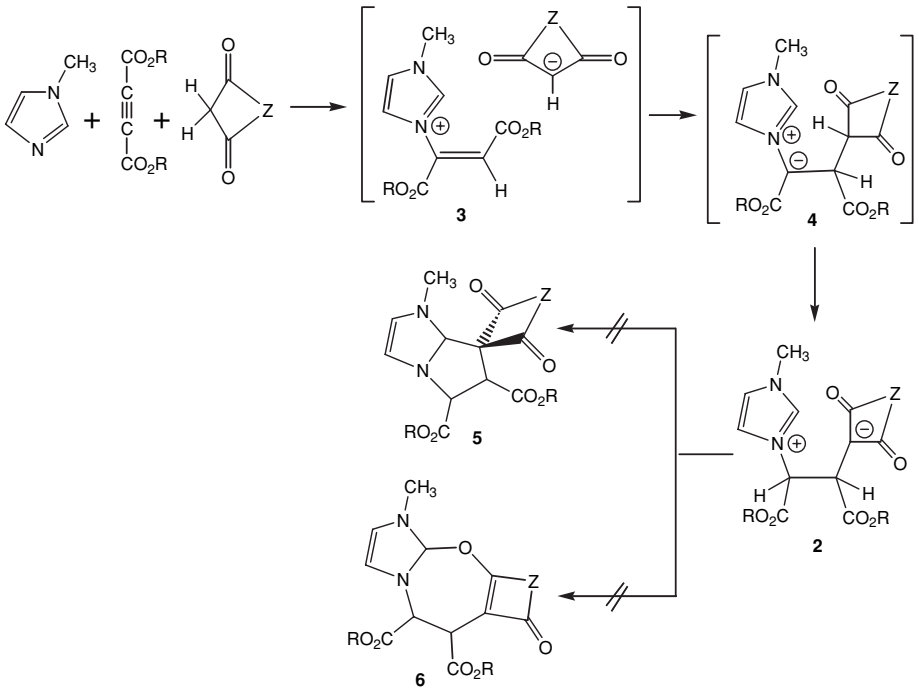


Scheme 3

subsequent protonation of the reactive 1:1 adduct by the CH-acid leads to vinylimidazolium cation **3** which undergoes an addition reaction with the enolate anion of the CH-acid to produce the nitrogen ylide **4**. This ylide apparently can be isomerised under the reaction conditions employed to produce the stable 1,4-diionic imidazolium betaines **2**. The cyclic products **5** or **6** are not formed from the intramolecular addition of carbon or oxygen atom to the imidazolium moiety.

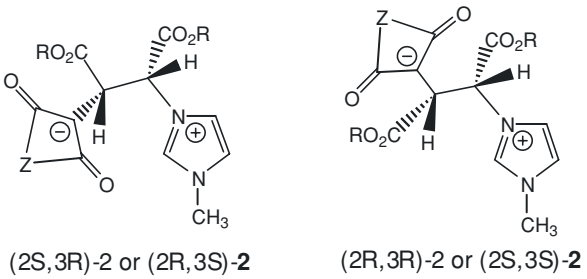
NMR spectroscopy was employed to distinguish **2** from the cyclic products **5** and **6**. The ^{1}H NMR of each of isolated product showed two methine proton (RO_2CCH–$CHCO_2R$) signals at about 4.22–4.94 and 5.20–5.88 ppm (doublets, $^3J_{HH}$=3.9–4.5 Hz). The H-4 and H–5 (NCH=CHN) protons of imidazolium moiety displayed signals 6.92–7.53 ppm and the H–2 (N-CH=N$^+$) protons resonated at 8.68-9.05 ppm.

The vicinal proton-proton coupling constant ($^3J_{HH}$) as a function of torsion angle can be obtained from the Karplus equation.[18] Typically, J_{gauche} varies between 1.5 and 5 Hz and J_{anti} between 10 and 14 Hz. Observation of $^3J_{HH}$= 3.9-4.5 Hz for the vicinal protons in compounds **2a**–**f** indicates a gauche arrangement for these centres. Since compound **2** possesses two stereogenic centres, two diastereoisomers with gauche HCCH arrangements are possible (Scheme 4). The ^{1}H NMR of the crude products **2a**–**f** were consistent with the presence of only one diastereomer (see Experimental).

In conclusion, we have found that the reaction of strong CH-acids, such as *N,N′*-dimethylbarbituric acid, Meldrum's acid, 1,3-cyclohexadione, 1,3-indandione, 1,3-cyclopentadione and tetronic acid with dialkyl acetylenedicarboxylate in the presence of 1-methylimidazole leads to a facile synthesis of highly functionalised stable 1,4-diionic imidazolium betaines **2a–f** in excellent fields. The present method carries the advantages that, not only is the reaction performed under neutral conditions, but the substances can be mixed without any activation or modification.

Experimental

Melting points were measured on a BÜCHI 535 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker DRX-400 Avance spectrometer at 400.13 and 100.77 MHz, respectively. The products **2a–f** are very soluble in water thus, ^{1}H and ^{13}C NMR spectra were obtained on solutions in D_2O. The reagents and solvents used in this work were purchased from Fluka (Buchs, Switzerland) chemical company and used without further purification.



(2S,3R)-2 or (2R,3S)-**2** (2R,3R)-2 or (2S,3S)-**2**

Scheme 4

Typical procedure for preparation of 5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-methoxycarbonylethyl]-1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-ide (**2a**): To a magnetically stirred solution of 1-methylimidazole (0.090 g, 1.1 mmol) and N,N'-dimethylbarbituric acid (0.156 g, 1.0 mmol) in ethyl acetate (5 ml) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.142 g, 1.0 mmol) in ethyl acetate (2 ml) at room temperature over 10 min. The reaction mixture was then allowed to stir at room temperature for 2 h. The precipitate was filtered and washed with diethyl ether (20 ml) to yield **2a** as a cream powder (0.369 g, 97%). M.p. 188–190 °C. IR (KBr) (ν_{max}, cm^{-1}): 1732, 1675, 1583, 1425. ^{1}H NMR (400 MHz, D_2O): δ_H 3.14 (6 H, s, 2 NCH_3), 3.70 (3 H, s, NCH_3), 3.83 and 3.88 (6 H, 2 s, 2 OCH_3), 4.94 (1 H, d, $^3J_{HH}$ = 4.1 Hz, CH–C(CO)$_2$), 5.20 (1 H, d, $^3J_{HH}$ = 4.1 Hz, CH–N$^+$), 6.92 and 7.09 (2 H, 2 nearly br s, NCH=CHN), 9.03 (1 H, s, N–CH=N$^+$). ^{13}C NMR (100 MHz, D_2O): δ_C 27.13 (2 NCH_3), 36.10 (NCH_3), 45.28 (CH-C(CO)$_2$), 52.13 and 53.02 (2 OCH_3), 62.91 (CH-N$^+$), 80.31 (C(CO)$_2$), 120.42 and 125.06 (NCH=CHN), 139.12 (N-CH=N$^+$), 153.24 (NCON), 162.51 (2 × NC=O), 167.82 and 174.40 (2 C=O of ester groups). MS (m/z, %): 380 (M$^+$, 3), 348 (10), 299 (14), 266 (46), 239 (52), 207 (12), 181 (46), 83 (100), 82 (96), 54 (20). Anal. Calcd for C_{16} $H_{20}N_4O_7$ (380.353): C, 50.52; H, 5.30; N, 14.73%. Found: C, 50.45; H, 5.33; N, 14.80%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-methoxycarbonylethyl]-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**2b**): White powder (0.350 g, 95%). M.p. 181–182 °C. IR (KBr) (ν_{max}, cm^{-1}): 1735, 1703, 1665, 1594. ^{1}H NMR (400 MHz, D_2O): δ_H 1.59 (6 H, s, CMe_2), 3.70 (3 H, s, NCH_3), 3.83 and 3.90 (6 H, 2 s, 2 OCH_3), 4.71 (1 H, d, $^3J_{HH}$ = 4.0 Hz, CH–C(CO)$_2$), 5.34 (1 H, d, $^3J_{HH}$ = 4.0 Hz, CH–N^+), 7.03 and 7.28 (2 H, 2 nearly br s, NCH=CHN), 8.94 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 25.67 (CMe_2), 36.50 (NCH_3), 45.76 (*C*H–C(CO)$_2$), 52.61 and 53.28 (2 OCH_3), 63.07 (CH–N^+), 69.06 (*C*(CO)$_2$), 101.65 (*C*Me_2), 120.31 and 125.16 (NCH=CHN), 139.37 (N–CH=N^+), 166.38 (2 C=O of ring), 168.20 and 174.83 (2 C=O of ester groups). MS (*m*/*z*, %): 368 (M^+, 2), 315 (7), 267 (12), 207 (33), 156 (31), 83 (100), 82 (97), 43 (70). Anal. Calcd for $C_{16}H_{20}N_2O_8$ (368.339): C, 52.17; H, 5.47; N, 7.61%. Found: C, 52.22; H, 5.51; N, 7.58%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-methoxycarbonylethyl]-2,6-dioxocyclohexane-1-ide (**2c**): Cream powder (0.250 g, 74%). M.p. 145–146 °C. IR (KBr) (ν_{max}, cm^{-1}): 1726, 1706, 1572, 1498. ^{1}H NMR (400 MHz, D_2O): δ_H 1.17 (2 H, q, $^3J_{HH}$ = 6.1 Hz, CH_2–*C*H_2–CH_2), 2.13 (4 H, t, $^3J_{HH}$ = 6.1 Hz, *C*H_2–CH_2–*C*H_2), 3.62 (3 H, s, NCH_3), 3.82 and 3.83 (6 H, 2 s, 2 OCH_3), 4.71 (1 H, d, $^3J_{HH}$ = 4.2 Hz, CH–C(CO)$_2$), 5.71 (1 H, d, $^3J_{HH}$ = 4.2 Hz, CH–N^+), 7.03 and 7.36 (2 H, 2 nearly br s, NCH=CHN), 8.68 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 20.71 (CH_2–*C*H_2–CH_2), 34.70 (*C*H_2–CH_2–*C*H_2), 35.94 (NCH_3), 42.53 (*C*H–C(CO)$_2$), 52.86 and 53.83 (2 OCH_3), 60.55 (CH–N^+), 106.43 (*C*(CO)$_2$), 122.47 and 133.35 (NCH=CHN), 136.83 (N–CH=N^+), 169.61 and 175.04 (2 C=O of ester groups), 195.51 (2 C=O of ring). MS (*m*/*z*, %): 336 (M^+, 5), 245 (11), 222 (61), 194 (51), 162 (100), 134 (65), 82 (27), 55 (24). Anal. Calcd for $C_{16}H_{20}N_2O_6$ (336.340): C, 57.14; H, 5.99; N, 8.33%. Found: C, 57.08; H, 6.04; N, 8.35%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-methoxycarbonylethyl]-1,3-dioxoindan-2-ide (**2d**): Dark yellow powder (0.356 g, 96%). M.p. 141–142 °C. IR (KBr) (ν_{max}, cm^{-1}): 1730, 1704, 1568, 1477. ^{1}H NMR (400 MHz, D_2O): δ_H 3.71 (3 H, s, NCH_3), 3.84 and 3.88 (6 H, 2 s, 2 OCH_3), 4.76 (1 H, d, $^3J_{HH}$ = 4.5 Hz, CH–C(CO)$_2$), 5.26 (1 H, d, $^3J_{HH}$ = 4.5 Hz, CH–N^+), 6.91 and 7.27 (2 H, $^3J_{HH}$ = 1.0 Hz, NCH=CHN), 7.24–7.26 (4 H, m, C_6H_4), 9.05 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 36.53 (NCH_3), 43.09 (*C*H–C(CO)$_2$), 52.73 and 53.43 (2 OCH_3), 63.54 (CH–N^+), 97.44 (*C*(CO)$_2$), 117.71, 129.67 and 139.03 (C_6H_4), 120.40 and 125.14 (NCH=CHN), 139.45 (N–CH=N^+), 167.84 and 175.15 (2 C=O of ester groups), 189.80 (2 C=O of ring). MS (*m*/*z*, %): 370 (M^+, 5), 354 (19), 323 (30), 256 (73), 228 (48), 197 (21), 170 (26), 146 (28), 82 (100), 55 (10). Anal. Calcd for $C_{19}H_{18}N_2O_6$ (370.356): C, 57.14; H, 5.99; N, 8.33%. Found: C, 57.08; H, 6.04; N, 8.35%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-methoxycarbonylethyl]-2,5-dioxocyclopentan-1-ide (**2e**): Cream powder (0.229 g, 71%). M.p. 151–152 °C. IR (KBr) (ν_{max}, cm^{-1}): 1730, 1704, 1568, 1477. ^{1}H NMR (400 MHz, D_2O): δ_H 2.22 (4 H, s, 2 CH_2), 3.67 (3 H, s, NCH_3), 3.83 and 3.84 (6 H, 2 s, 2 OCH_3), 4.30 (1 H, d, $^3J_{HH}$ = 3.9 Hz, CH–C(CO)$_2$), 5.88 (1 H, d, $^3J_{HH}$ = 3.9 Hz, CH–N^+), 7.34 and 7.42 (2 H, 2 nearly br s, NCH=CHN), 8.75 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 31.83 (2 CH_2), 35.92 (NCH_3), 42.05 (*C*H–C(CO)$_2$), 53.04 and 54.07 (2 OCH_3), 60.25 (CH–N^+), 105.73 (*C*(CO)$_2$), 122.51 and 123.22 (NCH=CHN), 137.24 (N–CH=N^+), 168.90 and 173.11 (2 C=O of ester groups), 204.55 (2 C=O of ring). MS (*m*/*z*, %): 322 (M^+, 2), 240 (14), 209 (27), 181 (28), 149 (33), 122 (10), 82 (100), 55 (24). Anal. Calcd for $C_{15}H_{18}N_2O_6$ (322.313): C, 55.90; H, 5.63; N, 8.69%. Found: C, 55.95; H, 5.60; N, 8.74%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-methoxycarbonylethyl]-2,4-dioxotetrahydrofuran-3-ide (**2f**): White powder (0.266 g, 82%). M.p. 144–146 °C. IR (KBr) (ν_{max}, cm^{-1}): 1730, 1700, 1562, 1427. ^{1}H NMR (400 MHz, D_2O): δ_H 3.58 (3 H, s, NCH_3), 3.69 and 3.73 (6 H, 2 s, 2 OCH_3), 4.20 (2 H, s, OCH_2), 4.22 (1 H, d, $^3J_{HH}$ = 4.5 Hz, CH–C(CO)$_2$), 5.80 (1 H, d, $^3J_{HH}$ = 4.5 Hz, CH–N^+), 7.25 and 7.53 (2 H, d, $^3J_{HH}$ = 1.5 Hz, NCH=CHN), 9.03 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 36.78 (NCH_3), 41.17 (*C*H–C(CO)$_2$), 52.79 and 54.02 (2 OCH_3), 61.33 (CH–N^+), 68.49 (OCH_2), 104.11 (*C*(CO)$_2$), 121.51 and 124.14 (NCH=CHN), 138.61 (N–CH=N^+), 167.14 and 175.08 (2 C=O of ester groups), 177.21 and 206.31 (2 C=O of ring). MS (*m*/*z*, %): 324 (M^+, 2), 211 (24), 180 (41), 152 (10), 83 (100), 82 (66). Anal. Calcd for $C_{14}H_{16}N_2O_7$ (324.286): C, 51.85; H, 4.97; N, 8.64%. Found: C, 51.91; H, 5.01; N, 8.66%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-ethoxycarbonylethyl]-1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-ide (**2g**): Cream powder (0.376 g, 92%). M.p. 171–173 °C. IR (KBr) (ν_{max}, cm^{-1}): 1736, 1668, 1570, 1421. ^{1}H NMR (400 MHz, D_2O): δ_H 1.19 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH_3 of ethyl), 1.28 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH_3 of ethyl), 3.16 (6 H, s, 2 NCH_3), 3.71 (3 H, s, NCH_3), 4.03–4.39 (4 H, m, 2 OCH_2), 4.95 (1 H, d, $^3J_{HH}$ = 4.0 Hz, CH–C(CO)$_2$), 5.18 (1 H, d, $^3J_{HH}$ = 4.0 Hz, CH–N^+), 6.88 and 7.15 (2 H, 2 nearly br s, NCH=CHN), 8.98 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 13.95 and 14.07 (2 CH_3), 27.15 (2 NCH_3), 36.03 (NCH_3), 45.41 (*C*H–C(CO)$_2$), 61.66 and 63.12 (2 OCH_2), 61.94 (CH–N^+), 80.45 (*C*(CO)$_2$), 120.38 and 125.19 (NCH=CHN), 139.01 (N–CH=N^+), 153.11 (NCON), 162.42 (2 NC=O), 166.72 and 174.51 (2 C=O of ester groups). MS (*m*/*z*, %): 408 (M^+, 2), 380 (7), 335 (15), 327 (19), 255 (23), 168 (41), 83 (100), 82 (93), 54 (17). Anal. Calcd for $C_{18}H_{24}N_4O_7$ (408.406): C, 52.94; H, 5.92; N, 13.72%. Found: C, 52.88; H, 5.90; N, 13.68%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-ethoxycarbonylethyl]-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**2h**): White powder (0.369 g, 93%). M.p. 177–179 °C. IR (KBr) (ν_{max}, cm^{-1}): 1730, 1699, 1653, 1588. ^{1}H NMR (400 MHz, D_2O): δ_H 1.20 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH_3 of ethyl), 1.31 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH_3 of ethyl), 1.61 (6 H, s, CMe_2), 3.71 (3 H, s, NCH_3), 4.08–4.42 (4 H, m, 2 OCH_2), 4.72 (1 H, d, $^3J_{HH}$ = 4.1 Hz, CH–C(CO)$_2$), 5.30 (1 H, d, $^3J_{HH}$ = 4.1 Hz, CH–N^+), 6.98 and 7.25 (2 H, 2 nearly br s, NCH=CHN), 9.04 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 14.02 and 14.09 (2 CH_3), 25.68 (CMe_2), 36.48 (NCH_3), 45.71 (*C*H–C(CO)$_2$), 61.11 and 63.06 (2 OCH_2), 64.21 (CH–N^+), 70.13 (*C*(CO)$_2$), 101.15 (*C*Me_2), 121.14 and 125.20 (NCH=CHN), 139.31 (N–CH=N^+), 167.44 (2 C=O of ring), 167.69 and 174.66 (2 C=O of ester groups). MS (*m*/*z*, %): 396 (M^+, 4), 351 (15), 323 (18), 268 (32), 225 (29), 169 (31), 83 (100), 82 (61), 43 (53). Anal. Calcd for $C_{18}H_{24}N_2O_8$ (396.392): C, 54.54; H, 6.10; N, 7.07%. Found: C, 54.47; H, 6.06; N, 7.10%.

5-[2-(1-methyl-1H-imidazol-3-ium-3-yl)-1,2-ethoxycarbonylethyl]-1,3-dioxoindan-2-ide (**2i**): Dark yellow powder (0.359 g, 90%). M.p. 156–158 °C. IR (KBr) (ν_{max}, cm^{-1}): 1740, 1700, 1562, 1473. ^{1}H NMR (400 MHz, D_2O): δ_H 1.18 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH_3 of ethyl), 1.29 (3 H, t, $^3J_{HH}$ = 7.1 Hz, CH_3 of ethyl), 3.74 (3 H, s, NCH_3), 3.98–4.36 (4 H, m, 2 OCH_2), 4.69 (1 H, d, $^3J_{HH}$ = 4.2 Hz, CH–C(CO)$_2$), 5.22 (1 H, d, $^3J_{HH}$ = 4.2 Hz, CH–N^+), 6.95 and 7.33 (2 H, 2 nearly br s, NCH=CHN), 7.25–7.27 (4 H, m, C_6H_4), 9.01 (1 H, s, N–CH=N^+). ^{13}C NMR (100 MHz, D_2O): δ_C 14.16 and 14.26 (2 CH_3), 36.61 (NCH_3), 43.46 (*C*H–C(CO)$_2$), 60.91 and 63.43 (2 OCH_2), 63.71 (CH–N^+), 98.14 (*C*(CO)$_2$), 117.84, 130.02 and 140.11 (C_6H_4), 120.89 and 125.55 (NCH=CHN), 140.06 (N–CH=N^+), 166.84 and 175.22 (2 C=O of ester groups), 189.91 (2 C=O of ring). MS (*m*/*z*, %): 398 (M^+, 3), 353 (10), 308 (14), 298 (30), 253 (22), 146 (35), 170 (26), 146 (28), 82 (100), 55 (10). Anal. Calcd for $C_{21}H_{22}N_2O_6$ (398.409): C, 63.31; H, 5.57; N, 7.03%. Found: C, 63.28; H, 5.60; N, 6.98%.

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