Facile Routes to Alkoxymaleimides/Maleic Anhydrides[1]

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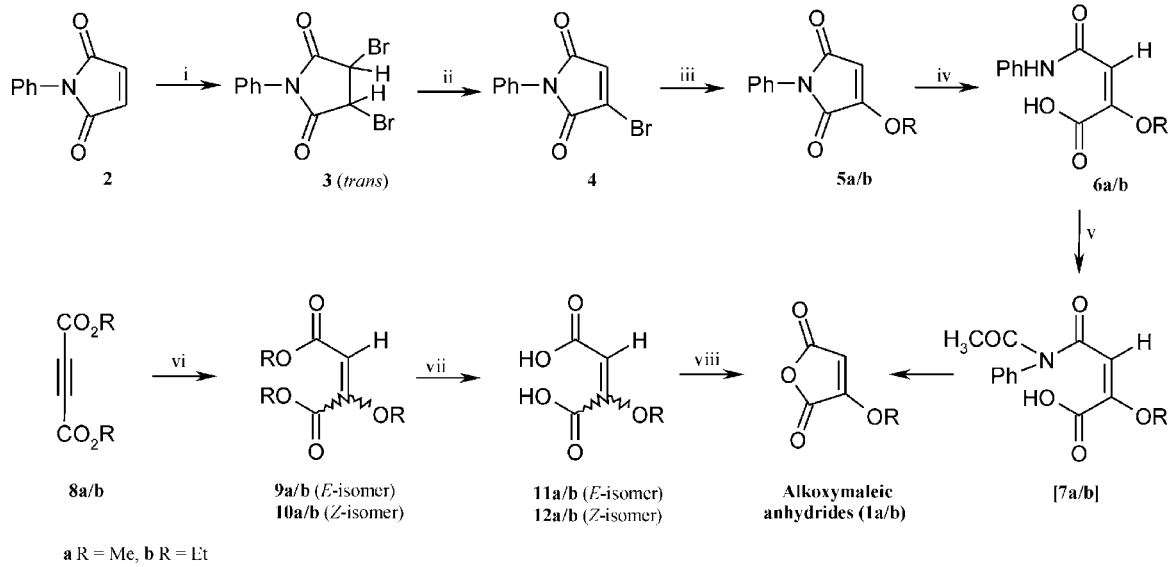
Abstract: New routes to alkoxymaleic anhydrides **1a**/**b** have been described in good yields via base-induced chemoselective vinylic substitution of bromo atom in bromomaleimide **4** with alkanols, and base-induced oxa-Micahel addition of alkanols to dialkyl acetylenedicarboxylates **8a**/**b** as key steps. An unusual acyl exchange in the conversion of **6a/b** to **1a/b** under very simple and mild reaction conditions is noteworthy.

Key words: bromomaleimide, dialkyl acetylenedicarboxylates, oxa-Michael additions, alkoxymaleic anhydrides

A very large number of applications of cyclic anhydrides are known in the literature. Alkoxy, alkoxyalkyl, alkoxyaryl and dialkoxymaleic anhydrides have been used for the synthesis of several bioactive natural products.[2] Methoxymaleic anhydride [3-methoxyfuran-2,5-dione (**1a**)] has been used for the synthesis of bioactive natural products narthigenine,[3] penicillic acid,[4,5] and lucidone.[6] Highly regioselective Wittig[7] reactions and metal hydride[8] reductions have been performed on **1a** to obtain precursors of bioactive natural products, the butyrolactones. The anhydride **1a** has been also used for the synthesis of benzothiazolylacrylic acid.[9] The corresponding methoxymaleimide has been used by Pattenden et al. for the synthesis of a constituent of the marine blue-green algae pukeleimide A.[10] To date two syntheses of methoxymaleic anhydride (**1a**) are known.[3,7b,11,12] The first synthesis[11] involves diazomethane-induced methylation of the enol of ethyl oxaloacetate as a key step. The second synthesis[12] has been completed by using diazomethane for methylation of the pyridine salt of hydroxymaleic anhydrides, which was obtained from tartaric acid in two steps. Both the above synthesis of **1a** use poisonous and explosive diazomethane for methylation reactions. Development of new, simple, general, and efficient routes to these potential building blocks, the cyclic anhydrides is a challenging task of current interest.[13] Very recently we have completed[14] a rapid access to alkoxysuccinic acids via oxa-Michael addition of alcohols to alkyl maleanilates, and in continuation of our ongoing programme[15] on the synthesis of several natural and unnatural cyclic anhydrides, we report herein reasoned and planned new routes to **1a**/**b**, using alkanols as a source of OR group (Scheme 1).



Scheme 1 *Reagents and conditions*: (i) Br_2, CCl_4, reflux, 1 h (98%); (ii) TEA, THF, 0 °C, 2 h (98%); (iii) Et_3N, ROH, reflux, 1 h (70–75%); (iv) (a) aq KOH, MeOH, r.t., 1 h, (b) H^+/HCl (96%); (v) Ac_2O–HOAc (1:1), 80 °C, 4 h (95%); (vi) Et_3N, ROH, r.t., 2 h (94–96%); (vii) (a) aq KOH, MeOH, r.t., 6 h, (b) H^+/HCl (93–96%); (viii) $SOCl_2$, reflux, 24 h (64–65%)

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The reaction of *N*-phenylmaleimide (**2**) with bromine in refluxing CCl_4 gave the *trans*-dibromosuccinimide **3** in quantitative yield.[16] Triethylamine-induced dehydrobromination of **3** at 0 °C yielded the bromomaleimide **4** in nearly 98% yield. The chemoselective base-catalyzed vinylic substitution of bromine atom in imide **4** with methanol/ethanol gave the alkoxymaleimides **5a**/**b** in 70–75% yields. The reaction of dibromosuccinimide **3** with Et_3N–MeOH also gave **5a**, but in 20–25% yield only. In our hands the compounds **5a**/**b** on acid-catalyzed hydrolysis (HCl, reflux, 1 h) underwent dealkylation reactions and furnished only decomposed/polymeric gums. The base-induced regioselective hydrolysis of **5a**/**b** at room temperature gave the corresponding maleanilic acids **6a**/**b** in quantitative yields. The cleavage of amide bond in anilic acids generally demands strong reaction conditions.[17] Remarkably the maleanilic acids **6a**/**b** in 1:1 mixture of acetic anhydride and acetic acid at 80 °C underwent a smooth acyl exchange reaction and furnished the mixture of acetanilide and desired alkoxymaleic anhydrides **1a**/**b** in 95% yield. We feel that, the present observed acyl exchange reaction is substrate, reagent and reaction conditions specific. The free carboxyl group, carbon–carbon double bond with *cis* geometry and acetic anhydride/acetic acid combination is necessary for the above acyl exchange reaction. We also feel that the present exchange reaction is plausibly taking place via the intermediate acyclic imides **7a**/**b**.

In our second approach we studied the base-induced oxa-Michael addition of alcohols to **8a**/**b** to obtain exclusively or in major amounts, the *E*-isomers of the dialkyl alkoxymaleates **9a**/**b**.[18] All our attempts using different temperatures and bases met with failure and we always got the **10a**/**b** as major products. The best yield of **9a**/**b** plus **10a**/**b** (94–96%) was obtained from the reaction of **8a**/**b** and alkanols using triethylamine as a base at room temperature in 2 hours (**9a**:**10a** = 30:70 and **9b**:**10b** = 20:80, by ^{1}H NMR spectroscopy). We could very easily separate these *E*- and *Z*-isomers **9a**/**b** and **10a**/**b** by silica gel column chromatography for characterization. Potassium hydroxide-catalyzed hydrolysis of *E*- and *Z*-mixture of ester **9a**/**b** and **10a**/**b** followed by acidification gave the corresponding mixture of acids **11a**/**b** and **12a**/**b** in 93–96% yields with same *E*:*Z* ratio. The pure esters **9a**/**b** and **10a**/**b** were also similarly hydrolyzed to corresponding acids **11a**/**b** and **12a**/**b** respectively. The mixture of acids **11a** plus **12a** and **11b** plus **12b** in refluxing thionyl chloride respectively furnished the desired alkoxymaleic anhydrides **1a** and **1b** in 64–65% yield. Both isomerization of *Z*-isomers **12a**/**b** to *E*-isomers **11a/b** and dehydrative ring-closure took place in one-pot.[6] The analytical and spectral data obtained for **1a/b** were in complete agreement with reported data.[11,12] The overall yield of **1a/b** in five steps (**2** to **1a**/**b**) and three steps (**8a**/**b** to **1a**/**b**) were 61–66% and 56–60% respectively. The one-step conversion of methoxymaleic anhydride (**1a**) to bioactive natural products narthigenine (antibiotic)[3] and penicillic acid (antimicrobial, antitumor, blood vessels dilation, antidiuretic)[4,19] are known.

In summary, we have demonstrated new general approaches to alkoxymaleic anhydrides via base induced vinylic substitution of bromo atom in **4** with alkanols and oxa-Michael addition of alkanols to dialkyl acetylenedicarboxylates **8a**/**b**. Such a chemoselective nucleophilic vinylic substitutions under very simple and mild reaction conditions will be useful in organic synthesis. The observed substrate, reagent and reaction conditions specific for an unusual acyl exchange reaction is noteworthy.

Melting points are uncorrected. ^{1}H NMR spectra were recorded on Bruker AC 200 NMR spectrometer (200 MHz) with TMS as an internal standard. Mass spectra were recorded on Finnigan Mat 1020 mass spectrometer at 70 eV. Column chromatographic separations were done on ACME silica gel (60–120 mesh). Petroleum ether with a bp range of 60–80 °C was used. Dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate were obtained from Aldrich Chemical Co. *N*-Phenylmaleimide (**2**) was prepared in quantitative yield using known procedure.[20]

***trans*-2,3-Dibromo-*N*-phenylsuccinimide (3)**

To a solution of *N*-phenylmaleimide (**2**; 1.73 g, 10 mmol) in CCl_4 (15 mL) was added dropwise a solution of Br_2 (0.57 mL, 11 mmol) in CCl_4 (10 mL) at r.t. After complete addition, the reaction mixture was refluxed for 1 h, and then allowed to cool to r.t. The precipitate was filtered and washed with CCl_4 (2 × 5 mL) and dried; yield: 3.26 g (98%); mp 155–157 °C.

IR (Nujol): 1798, 1728, 1591 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.87 (s, 2 H), 7.30–7.70 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 41.9, 44.4, 126.0, 129.4, 130.8, 130.9, 169.2, 169.5.

MS: *m*/*z* = 335, 333, 331, 253, 251, 196, 173, 144, 128, 119, 104, 91, 77.

Anal. Calcd for $C_{10}H_7Br_2NO_2$: C, 36.07; H, 2.12; N, 4.21. Found: C, 35.84; H, 2.19; N, 4.35.

2-Bromo-*N*-phenylmaleimide (4)

To a solution of **3** (3.0 g, 9 mmol) in THF (30 mL) was added dropwise a solution of Et_3N (1.38 mL, 9.9 mmol) in THF (5 mL) at 0 °C and the mixture was stirred for 2 h. The mixture was allowed to warm to r.t. and concentrated in vacuo. The residue was dissolved in EtOAc and washed with H_2O, brine and dried (Na_2SO_4). Concentration of the organic layer in vacuo furnished **4**; yield: 2.23 g (98%); mp 161–163 °C.

IR (Nujol): 1782, 1716, 1713, 1595 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.03 (s, 1 H), 7.30–7.60 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 126.0, 128.2, 129.1, 131.0, 131.7, 131.8, 164.1, 167.3.

MS: *m*/*z* = 253, 251, 211, 196, 171, 144, 128, 119, 104, 91, 77, 71, 64.

Anal. Calcd for $C_{10}H_6BrNO_2$: C, 47.65; H, 2.40; N, 5.56. Found: C, 47.71; H, 2.29; N, 5.50.

2-Methoxy-*N*-phenylmaleimide (5a)

To a solution of **4** (1.0 g, 3.97 mmol) in MeOH (10 mL) was added a solution of Et_3N (0.61 mL, 4.37 mmol) in MeOH (5 mL), and the reaction mixture was refluxed for 1 h. Concentration of the mixture in vacuo followed by silica gel column chromatographic purification of the residue using petroleum ether–EtOAc (8:2) as eluent gave **5a**; yield: 604 mg (75%); mp 99–101 °C.

IR (Nujol): 1778, 1730, 1715, 1643, 1599 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.02 (s, 3 H), 5.58 (s, 1 H), 7.25–7.55 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 58.9, 96.3, 125.9, 127.6, 128.9, 131.0, 160.6, 164.2, 168.8. MS: *m*/*z* = 203, 174, 147, 119, 105, 88, 84, 77, 69, 64, 59.

Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.90. Found: C, 65.19; H, 4.67; N, 6.76.

2-Ethoxy-*N*-phenylmaleimide (5b)
Repetition of above reaction with EtOH furnished **5b**; yield: 70%; mp 116–117 °C.

IR (Nujol): 1782, 1720, 1641, 1605 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.54 (t, *J* = 6 Hz, 3 H), 4.22 (q, *J* = 6 Hz, 2 H), 5.53 (s, 1 H), 7.25–7.60 (m, 5 H).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.11; N, 6.45. Found: C, 66.47; H, 5.02; N, 6.53.

2-Methoxymaleanilic Acid (6a)
To a solution of **5a** (500 mg, 2.46 mmol) in MeOH (5 mL) was added a solution of KOH (207 mg, 3.7 mmol) in H_2O (5 mL) and the reaction mixture was stirred for 1 h at r.t. The mixture was concentrated in vacuo and acidified with aq 10 N HCl at 0 °C. The precipitate formed was filtered and dried under vacuo; yield: 523 mg (96%); mp 184–185 °C.

IR (Nujol): 3265, 1730, 1653, 1612, 1460, 1321 cm^{-1}.

^{1}H NMR (methanol-d_4, 200 MHz): δ = 3.79 (s, 3 H), 5.75 (s, 1 H), 7.12 (t, *J* = 8 Hz, 1 H), 7.33 (t, *J* = 8 Hz, 2 H), 7.57 (d, *J* = 8 Hz, 2 H).

Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.61; H, 4.93; N, 6.19.

2-Ethoxymaleanilic Acid (6b)
The above reaction carried out in EtOH afforded **6b**; yield: 96%; mp 145–147 °C.

IR (Nujol): 3290, 1709, 1616, 1462 cm^{-1}.

^{1}H NMR (methanol-d_4, 200 MHz): δ = 1.41 (t, *J* = 8 Hz, 3 H), 3.97 (q, *J* = 8 Hz, 2 H), 5.69 (s, 1 H), 7.10 (t, *J* = 8 Hz, 1 H), 7.31 (t, *J* = 8 Hz, 2 H), 7.56 (d, *J* = 8 Hz, 2 H).

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.20; H, 5.69; N, 6.03.

Dimethyl Methoxymaleate/Dimethyl Methoxyfumarate (9a/10a)
To a stirred solution of dimethyl acetylenedicarboxylate (**8a**; 5.0 g, 35.21 mmol) in MeOH (50 mL) was added dropwise Et_3N (2.7 mL, 19.37 mmol) and the reaction mixture was stirred at r.t. for 2 h. Concentration of the mixture in vacuo followed by column chromatographic purification of the residue by silica gel column chromatography using petroleum ether–EtOAc (9:1) as eluent gave **9a** and **10a** in a total yield of 96%.

9a
Yield: 1.72 g (28%); thick oil.

IR ($CHCl_3$): 1753, 1720, 1630, 1439, 1371 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.71 (s, 3 H), 3.75 (s, 3 H), 3.89 (s, 3 H), 5.21 (s, 1 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 51.1, 52.4, 56.6, 92.7, 162.1, 163.5, 165.8.

MS: *m*/*z* = 174, 159, 143, 127, 115, 110, 101, 85, 69, 59, 53.

Anal. Calcd for $C_7H_{10}O_5$: C, 48.28; H, 5.79; Found: C, 48.35; H, 5.91.

10a
Yield: 4.17 g (68%); thick oil.

IR ($CHCl_3$): 1745, 1726, 1641, 1437, 1362, 1269 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.75 (s, 3 H), 3.84 (s, 3 H), 3.93 (s, 3 H), 6.18 (s, 1 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 51.1, 52.3, 60.5, 107.3, 154.4, 162.7, 164.2.

MS: *m*/*z* = 174, 159, 143, 127, 115, 110, 101, 84, 69, 59, 53.

Anal. Calcd for $C_7H_{10}O_5$: C, 48.28; H, 5.79; Found: C, 48.39; H, 5.97.

Diethyl Ethoxymaleate/Diethyl Ethoxyfumarate (9b/10b)
Similarly the reaction of **8b** with EtOH afforded **9b** (18%) and **10b** (76%) in a total of 94% yield.

9b
Yield : 18%; thick oil.

IR ($CHCl_3$): 1746, 1713, 1626, 1379, 1194 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.26 (t, *J* = 6 Hz, 3 H), 1.37 (t, *J* = 6 Hz, 3 H), 1.40 (t, *J* = 6 Hz, 3 H), 3.93 (q, *J* = 8 Hz, 2 H), 4.16 (q, *J* = 8 Hz, 2 H), 4.35 (q, *J* = 8 Hz, 2 H), 5.15 (s, 1 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.3, 13.4, 13.7, 59.7, 61.6, 65.5, 92.6, 161.7, 163.3, 165.4.

MS: *m*/*z* (%) = 216, 201, 187, 171, 143, 115, 99, 87, 69.

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46; Found: C, 55.64; H, 7.23.

10b
Yield: 76%; thick oil.

IR ($CHCl_3$): 1736, 1730, 1641, 1634, 1376, 1257 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.29 (t, *J* = 6 Hz, 3 H), 1.33 (t, *J* = 6 Hz, 3 H), 1.36 (t, *J* = 6 Hz, 3 H), 4.10–4.40 (m, 6 H), 6.18 (s, 1 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.8, 13.9, 15.1, 60.2, 61.8, 69.3, 109.2, 154.1, 162.8, 164.2.

MS: *m*/*z* = 216, 187, 171, 143, 115, 99, 87, 69.

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46; Found: C, 55.41; H, 7.48.

Methoxymaleic Acid (11a)
To a solution of **9a** (1.0 g, 5.75 mmol) in MeOH (15 mL) was added a solution aq 4 N KOH (15 mL) and the reaction mixture was stirred at r.t. for 6 h. The mixture was cooled to 0 °C and acidified with aq 10 N HCl till pH 2. The aqueous layer was extracted with Et_2O (5 × 20 mL) and the organic layer was washed with H_2O, brine and dried (Na_2SO_4). Concentration of organic layer in vacuo gave **11a**; yield: 780 mg (93%); mp 128–130 °C.

IR (Nujol): 1701, 1690, 1637, 1215 cm^{-1}.

^{1}H NMR (acetone-d_6, 200 MHz): δ = 3.81 (s, 3 H), 5.33 (s, 1 H).

^{13}C NMR (acetone-d_6, 50 MHz): δ = 57.4, 93.8, 164.0, 164.2, 168.0.

MS: *m*/*z* = 146, 128, 102, 87, 84, 69, 53.

Anal. Calcd for $C_5H_6O_5$: C, 41.11; H, 4.14; Found: C, 41.01; H, 4.19.

Compounds **12a**, **11b**, and **12b** were prepared similarly to **11a**. A mixture of **9a**/**b** and **10a**/**b** were also hydrolyzed to the corresponding mixture of acids.

Methoxyfumaric Acid (12a)
Yield: 95%; mp 141–143 °C.

IR (Nujol): 1702, 1692, 1643, 1462, 1279, 1231 cm^{-1}.

^1H NMR (acetone-d_6, 200 MHz): δ = 3.92 (s, 3 H), 6.17 (s, 1 H).

^{13}C NMR (DMSO-d_6, 50 MHz): δ = 60.3, 108.7, 154.9, 164.2, 165.7.

MS: *m*/*z* = 146, 128, 110, 98, 87, 69, 59, 53.

Anal. Calcd for $C_5H_6O_5$: C, 41.11; H, 4.14; Found: C, 41.13; H, 4.19.

Ethoxymaleic Acid (11b)
Yield: 96% yield; mp 120–121 °C.

IR (Nujol): 1730, 1685, 1454, 1377 cm^{-1}.

^1H NMR (acetone-d_6, 200 MHz): δ = 1.36 (t, *J* = 8 Hz, 3 H), 4.02 (q, *J* = 8 Hz, 2 H), 5.28 (s, 1 H), 8.83 (br s, 2 H).

^{13}C NMR (acetone-d_6, 50 MHz): δ = 14.2, 66.6, 93.7, 163.6, 164.2, 167.9.

MS: *m*/*z* = 142, 116, 98, 87, 69, 57, 53.

Anal. Calcd for $C_6H_8O_5$: C, 45.01; H, 5.03; Found: C, 45.22; H, 5.10.

Ethoxyfumaric Acid (12b)
Yield: 96%; mp 117–118 °C.

IR (Nujol): 1722, 1685, 1423, 1269, 1215 cm^{-1}.

^1H NMR (acetone-d_6, 200 MHz): δ = 1.32 (t, *J* = 8 Hz, 3 H), 4.22 (q, *J* = 8 Hz, 2 H), 6.19 (s, 1H), 8.71 (br s, 2 H).

^{13}C NMR (acetone-d_6, 50 MHz): δ = 15.2, 69.8, 109.6, 154.9, 164.0, 165.6.

MS: *m*/*z* = 160, 151, 145, 139, 116, 98, 87, 69, 53.

Anal. Calcd for $C_6H_8O_5$: C, 45.01; H, 5.03; Found: C, 45.13; H, 5.11.

Methoxymaleic Anhydride (1a)
Method A: A mixture of **11a** and **12a** (3.5 g, 24 mmol) and $SOCl_2$ (50 mL) was stirred at 25 °C for 1 h and then refluxed for 24 h. The mixture was concentrated in vacuo and Kugelrohr distillation of the residue gave **1a** (1.96 g, 64%).

Method B: 2-Methoxymaleanilic acid (**6a**; 300 mg, 1.36 mmol) was heated at 80 °C in a mixture of HOAc and Ac_2O (1:1, 10 mL) for 4 h. Ac_2O and HOAc were distilled off in vacuo and the residue was purified by silica gel column chromatography using petroleum ether–EtOAc (8:2) as eluent to obtain **1a** (165 mg, 95%); mp 152–155 °C.

IR ($CHCl_3$): 1857, 1776, 1649, 1225 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 4.04 (s, 3 H), 5.78 (s, 1 H).

^{13}C NMR (acetone-d_6, 50 MHz): δ = 61.0, 99.8, 161.9, 163.0, 164.4.

Anal. Calcd for $C_5H_4O_4$: C, 46.89; H, 3.15; Found: C, 47.02; H, 3.18.

Ethoxymaleic Anhydride (1b)
Similarly **11b** and **12b** and **6b** gave **1b**; mp 127–128 °C.

IR ($CHCl_3$): 1760, 1730, 1645, 1618, 1443, 1215 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.53 (t, *J* = 8 Hz, 3 H), 4.24 (q, *J* = 8 Hz, 2 H), 5.71 (s, 1 H).

^{13}C NMR (acetone-d_6, 50 MHz): δ = 14.0, 70.8, 99.6, 161.9, 162.1, 164.6.

Anal. Calcd for $C_6H_6O_4$: C, 50.71; H, 4.26; Found: C, 50.82; H, 4.29.

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