Nitroalkanes and Dimethyl Maleate as Source of 3-Alkyl Succinic Anhydrides and (*E*)-3-Alkylidene Succinic Anhydrides

Roberto Ballini,*[a] Giovanna Bosica,[a] Dennis Fiorini,[a] Paolo Righi[b]

[a] Dipartimento di Scienze Chimiche dell'Università, Via S. Agostino 1, 62032 Camerino (MC), Italy
Fax +39(0737)402297; E-mail: roberto.ballini@unicam.it

[b] Dipartimento di Chimica Organica "A. Mangini" dell'Università, V.le Risorgimento 4, 40136 Bologna, Italy

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Dedicated to Ahlem Chamakh, a promising chemistry student in the field of nitro compounds (University of Tunis) who died 27 September 2001

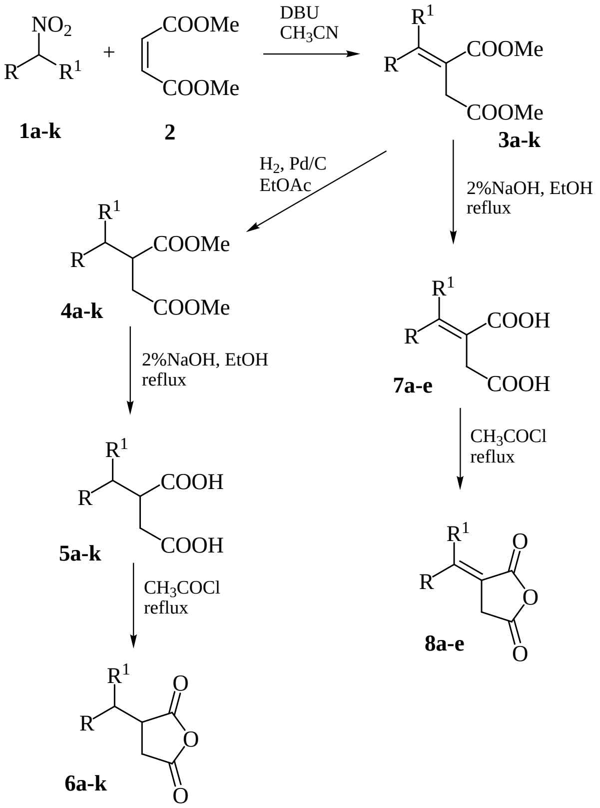
Abstract: Nitroalkanes react with dimethyl maleate giving a tandem Michael addition/elimination of nitrous acid. The obtained (*E*)-2-alkylidene dimethyl succinates are: (i) reduced to the corresponding 2-alkyl dimethyl succinates which after hydrolysis produce 1,4-dicarboxylic acids that are prone to convert into the corresponding 3-alkyl succinic anhydrides or (ii) hydrolysed to (*E*)-2-alkylidene-succinic acids that are easily cyclised to (*E*)-3-alkylidene succinic anhydrides.

Key words: nitroalkanes, 3-alkyl succinic anhydrides, 3-alkylidene succinic anhydrides, dimethyl maleate, heterocyclic compounds

3-Alkyl-dihydro-furan-2,5-diones (3-alkyl succinic anhydrides) and (*E*)-3-alkylidene-dihydro-furan-2,5-diones [(*E*)- 3-alkylidene succinic anhydrides] are both important class of compounds due to their utility as intermediates in the synthesis of important targets such as natural antibiotics,[1,2] pyrrolidines,[3] metalloproteinase inhibitors,[4] inhibitors towards human leukocytes,[5] cephalotaxine,[6] and monoesters of alkylated succinic acids.[7] Although several methods have been reported[3–7,8–12] for the preparation of the title compounds, they seem not of general applicability.

Recently, an interesting methodology for the preparation of 3-alkyl succinic anhydrides has been published.[7d] However, a more efficient procedure for the synthesis of both the anhydrides is still desirable.

Over the last decade aliphatic nitro compounds have demonstrated to be a valuable source for the preparation of alkylated heterocyclic derivatives.[13] In continuation of our studies we wish to report here a general synthesis of both 3-alkyl succinic anhydrides **6** and (*E*)-3-alkylidene succinic anhydrides **8**, using nitroalkanes **1** and dimethyl maleate **2** as common starting materials. Conjugate addition (Scheme) of the nitronate, derived from the nitro compound **1**, to **2** in acetonitrile with DBU as base allows the formation of the product **3**, essentially as single stereoisomer of *E* configuration.[13a,14] The adduct **3** is obtained pure enough and can be directly used without purification as the key building block for the synthesis of the anhydrides **6** or **8** by two different synthetic sequences.



Scheme Synthesis of compounds **6a**–**k** and **8a**–**e**.

Thus, chemoselective hydrogenation (10% Pd/C as catalyst) of the C=C double bond of the crude compound **3** yields the saturated diester **4** (80–98% from **1**). Saturated diester **4** after hydrolysis with aqueous 2% sodium hydroxide and ethanol at reflux temperature provides the dicarboxylic acid **5** (63–90%).

Although several methods are available for the conversion of 1,4-dicarboxylic acids into the corresponding anhydrides, we chose acetyl chloride[15] as a dehydrating agent for the preparation of **6** in high yields (85–98%, Table 1). On the other hand, the basic hydrolysis of the crude adduct **3** (2% sodium hydroxide solution) allows the formation of the 2-alkylidene succinic acid **7** (71–95%). The 2-alkylidene succinic acids **7** are converted to the (*E*)-2-alkylidene succinic anhydrides **8** in excellent yield (87–98%) following the previous procedure for the anhydrides **6**.

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Table 1 Synthesis of 3-Alkyl Succinic Anhydrides **6** and (*E*)-3-Alkylidene Succinic Anhydrides **8**

			Yield (%)[a] of				
Entry	R	R^1	**4**	**5**	**6**	**7**	**8**
a	$(CH_3)_2CH$	H	92	68	98	86	98
b	$CH_3COCH_2CH_2$	H	91	63	90	82	87
c	$(CH_3)_2CHCH_2$	H	98	80	89	95	91
d	CH_3CH_2	H	80	83	96	71	97
e	$HOCH_2(CH_2)_4$	H	96	77	95[b]	73	98[b]
f	$CH_3(CH_2)_3$	H	86	90	95		
g	$PhCH_2$	H	95	88	98		
h	$CH_2(CH_2)_3CH_2$	H	98	88	89		
i	$CH_3(CH_2)_9$	H	88	88	96		
j	$CH_3CO(CH_2)_2$	CH_3	87	69	89		
k	Ph	H	98	75	85		

[a] Yield of isolated purified product.

[b] R group for **6e** and **8e** is $CH_3COO(CH_2)_5$.

In conclusion, we have demonstrated that nitroalkanes can be conveniently employed for a general synthesis of 3-alkyl succinic anhydrides and for the stereoselective preparation of (*E*)-3-alkylidene succinic anhydrides. Moreover, this methodology allows different, important functionalities to be introduced by using simple procedures and cheap economical starting materials.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200 and 75 MHz, respectively on a Varian Gemini 200 MHz instrument. Chemical shifts are expressed in ppm downfield from TMS. Mass spectra were determined on a capillary GC/MS operating in the split mode with He carrier gas with a mass-selective detector (MDS). IR spectra were recorded with a Perkin Elmer 257 spectrophotometer. Elemental analyses were performed using a C, H Analyser Model 185 from Hewlett Packard. All the reactions were monitored by TLC and gas chromatographic analyses, performed on a Carlo Erba Fractovap 4160 using a capillary column of Duran glass (0.32 mm × 25 m), stationary phase OV1 (film thickness 0.4–0.45 µm).

Adducts (4a–k); General Procedure

To a solution of nitroalkane **1** (10 mmol) and dimethyl maleate **2** (10 mmol) in CH_3CN (30 mL) DBU (10 mmol) was added at r.t. The solution was then stirred for 5 h and evaporated. The crude residue was dissolved in CH_2Cl_2 (10 mL), washed with 2 N HCl (2 × 10 mL), dried over Na_2SO_4 and evaporated. To the obtained product **3**, EtOAc (6 mL; 0.1 g = solvent/substrate) and 10% Pd/C (0.2 g) were added and the suspension was hydrogenated (40 psi) at r.t. for 6 h. The catalyst was removed by filtration through a bed of Celite and washed with EtOAc (3 × 20 mL). After evaporation of the solvent the crude product **4** was purified by flash chromatography (petroleum ether–EtOAc). For spectroscopic data see Table 2.

2-Alkyl Succinic Acids (5a–k) and 2-Alkylidene Succinic Acids (7a–e); General Procedure

The compound **3** or **4** (2.6 mmol) was dissolved in EtOH (10 mL) and 2% NaOH (50 mL) was added. The solution obtained was refluxed for 5 h then concentrated to 1/3 of the volume. H_2O (100 mL) was added and the solution was washed with EtOAc (3 × 10 mL). The water phase was acidified to pH 1 with 2 N HCl (5 mL), extracted with EtOAc (3 × 20 mL), washed with brine (20 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvent the crude product was purified by flash chromatography using petroleum ether–EtOAc as the mobile phase to give the pure dicarboxylic acids **5** and **7**. For spectroscopic data see Table 3 and Table 4.

3-Alkyl Succinic Anhydrides (6a–k) and (*E*)-3-Alkylidene Succinic Anhydrides (8a–e); General Procedure

A mixture of succinic acid **5** or **6** (2 mmol) and acetyl chloride (15 mmol) was refluxed for 3 h. The solution was then concentrated to give the 3-alkyl succinic anhydride **6** and 3-alkylidene succinic anhydride **8** as pure compounds (GC >98%). For spectroscopic data see Table 5 and Table 6.

Table 2 Spectroscopic Data for Adducts **4a**–**k**

Product	IR (film) (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm), *J* (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)
4a	1740	0.9 (d, 3 H, *J* = 6.2), 0.94 (d, 3 H, *J* = 7.3), 1.28–1.40 (m, 2 H), 1.50–1.68 (m, 1 H), 2.43 (dd, 1 H, *J* = 5.1, 16.5), 2.7 (dd, 1 H, *J* = 9.5, 16.5), 2.84–3.0 (m, 1 H), 3.68 (s, 3 H), 3.71 (s, 3 H)	175.2, 171.94, 51.63, 51.40, 41.60, 39.60, 36.38, 26.20, 22.55
4b	1732	1.5–1.7 (m, 4 H), 2.15 (s, 3 H), 2.38–2.53 (m, 3 H), 2.65–2.9 (m, 2 H), 3.68 (s, 3 H), 3.71 (s, 3 H)	209.12, 176.4, 172.5, 51.70, 51.63, 44.29, 39.54, 35.96, 30.45, 29.98, 22.21
4c	1740	0.84 (d, 6 H, *J* = 6.4), 1.15 (dd, 2 H, *J* = 7.0, 15.9), 1.4–1.68 (m, 3 H), 2.42 (dd, 1 H, *J* = 4.6, 16.2), 2.6–2.85 (m, 2 H), 3.64 (s, 3 H), 3.68 (s, 3 H)	176.1, 172.09, 51.72, 51.63, 39.68, 37.95, 35.91, 31.27, 27.34, 23.10
4d	1738	0.92 (t, 3 H, *J* = 6.7), 1.25–1.4 (m, 2 H), 1.4–1.7 (m, 2 H), 2.45 (dd, 1 H, *J* = 4.8, 16.1), 2.76 (d, 1 H, *J* = 16.1), 2.63–2.96 (m, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H)	175.05, 172.10, 51.63, 51.40, 41.50, 36.20, 34.7, 20.58, 14.00
4e	3448, 1736	1.22–1.42 (m, 6 H), 1.44–1.78 (m, 4 H), 2.38–2.5 (m, 1 H), 2.64–2.8 (m, 1 H), 2.8–2.93 (m, 1 H), 3.64 (t, 2 H, *J* = 6.4), 3.68 (s, 3 H), 3.7 (s, 3 H)	175.5, 172.5, 62.78, 51.70, 51.63, 41.30, 35.90, 32.43, 29.89, 29.40, 26.90, 26.12,

Table 2 Spectroscopic Data for Adducts **4a**–**k** (continued)

Product	IR (film) (cm^{-1})	^{1}H NMR ($CDCl_3$) δ (ppm), J (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)
4f	1736	0.82 (t, 3 H, J = 7.2), 1.16–1.30 (br s, 6 H), 1.4–1.48 (m, 1 H), 1.5–1.62 (m, 1 H), 2.33–2.42 (m, 1 H), 2.6–2.86 (m, 2 H), 3.62 (s, 3 H), 3.65 (s 3 H)	175.49, 172.47, 51.76, 51.72, 41.14, 35.79, 31.88, 31.51, 26.56, 22.39, 13.93
4g	1717, 1603	1.78–2.1 (m, 2 H), 2.41–2.95 (m, 5 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 7.1–7.35 (m, 5 H)	176.5, 174.8, 142.6, 129.1, 128.0, 125.7, 51.7, 51.5, 43.7, 34.2, 31.4, 28.8
4h	1732	0.96–1.3 (m, 6 H), 1.5–1.8 (m, 5 H), 2.38–2.54 (m, 1 H), 2.62–2.78 (m, 2 H), 3.66 (s, 3 H), 3.7 (s, 3 H)	176.9, 174.3, 51.6, 51.1, 42.5, 37.3, 33.7, 31.7, 30.0, 27.3, 26.8
4i	1739	0.9 (t, 3 H, J = 7.6), 1.27 (br s, 20 H), 2.35–2.5 (m, 1 H), 2.62–2.9 (m, 2 H), 3.68 (s, 3 H), 3.71 (s, 3 H)	175.5, 172.6, 51.70, 51.63, 41.30, 35.90, 31.97, 29.80, 29.78, 29.63, 29.55, 29.40, 29.36, 29.16, 26.77, 22.69, 14.10
4j	1732	0.88 (d, 3 H, J = 6.9), 1.2–1.8 (m, 3 H), 2.18 (s, 3 H), 2.28–2.48 (m, 3 H), 2.67–2.96 (m, 2 H), 3.68 (s 3 H), 3.71 (s, 3 H)	208.59, 173.6, 173.53, 51.7, 51.5, 44.80, 43.34, 36.28, 33.71, 29.87, 24.58, 18.46
4k	1718, 1604	2.4–2.94 (m, 5 H), 3.67 (s, 3 H), 3.62 (s, 3 H), 7.14–7.27 (m, 5 H)	174.73, 173.41, 139.52, 128.21, 128.00, 127.62, 51.65, 51.63, 41.87, 37.00, 34.71

Table 3 Spectroscopic Data for 2-Alkyl Succinic Acids **5a**–**k**

Product	IR (film) (cm^{-1})	^{1}H NMR ($CDCl_3$) δ (ppm), J (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)
5a	1714	0.93 (d, 3 H, J = 6.2), 0.96 (d, 3 H, J = 6.2), 1.22–1.48 (m, 1 H), 1.58–1.77 (m, 2 H), 2.42–2.58 (m, 1 H), 2.6–2.79 (m, 1 H), 2.81–3.0 (m, 1 H), 11 (br s, 2 H)	181.85, 178.54, 40.81, 39.24, 35.99, 25.63, 22.36, 22.24
5b	1710	1.43–1.8 (m, 4 H), 2.18 (s, 3 H), 2.4–2.6 (m, 3 H), 2.63–2.97 (m, 2 H), 7.5 (br s, 2 H)	209.28, 180.28, 177.53, 43.20, 40.89, 35.59, 31.02, 30.12, 21.06
5c	1690	0.90 (d, 6 H, J = 6.6), 1.18–1.33 (m, 2 H), 1.45–1.82 (m, 3 H), 2.52 (dd, 1 H, J = 15.4, 2.9), 2.78 (d, 1 H, J = 15.4), 2.66–2.93 (m, 1 H), 9.6 (br s, 2 H)	181.37, 178.41, 41.15, 35.85, 35.51, 29.53, 27.90, 22.41, 22.37
5d	1702	0.94 (t, 3 H, J = 7.1), 1.34–1.82 (m, 4 H), 2.52 (dd, 1 H, J = 16.8, 3.7), 2.66–2.82 (m, 1 H), 2.82–2.96 (m, 1 H)	181.63, 178.66, 40.88, 35.64, 33.74, 20.11, 13.78
5e	1709	1.2–1.6 (m, 10 H), 2.22–2.4 (m, 2 H), 2.45–2.62 (m, 1 H), 3.38 (t, 2 H, J = 6.4), 4.38 (br s, 1 H), 12.1 (br s, 1 H)	175.96, 173.11, 60.60, 40.58, 35.54, 32.34, 31.25, 28.71, 26.34, 25.23
5f	1705	0.8–0.95 (m, 3 H), 1.2–1.48 (m, 6 H), 1.5–1.8 (m, 2 H), 2.43–2.92 (m, 3 H)	181.59, 178.62, 41.02, 35.57, 31.61, 31.49, 26.51, 22.38, 13.96
5g	3645, 3625, 1694, 1602	1.15–1.3 (m, 2 H), 1.78–1.96 (m, 1 H), 1.98–2.1 (m, 1 H), 2.5–2.82 (m, 2 H), 2.84–3.0 (m, 1 H), 7.12–7.4 (m, 5 H)	180.75, 177.85, 140.70, 128.52, 128.40, 126.21, 40.84, 35.63, 33.26, 33.07
5h	1698	1.0–1.4 (m, 6 H), 1.58–1.91 (m, 5 H), 2.41–2.63 (m, 1 H), 2.64–2.86 (m, 2 H), 9.5 (br s, 2 H)	181.05, 179.20, 47.00, 39.57, 33.10, 30.74, 29.83, 26.27, 26.24, 26.05
5i	1694	0.84 (t, 3 H, J = 6.7), 1.2–1.38 (br s, 18 H), 1.4–1.58 (m, 1 H), 1.60–1.78 (m, 1 H), 2.43–2.57 (m, 1 H), 2.64–2.89 (m, 2 H)	181.32, 178.34, 41.10, 35.64, 31.90, 31.66, 29.69, 29.59, 29.54, 29.33, 29.07, 28.94, 26.87, 22.67, 14.10
5j	1714	0.78 (d, 1.8 H, J = 6.7), 0.85 (d, 1.2 H, J =6.7), 1.2–1.6 (m, 3 H), 1.92 (s, 1.2 H), 2.08 (s, 1.8 H), 2.21–2.67 (m, 5 H), 12.1 (br s, 2 H)	208.19, 208.12, 175.34, 174.87, 173.55, 173.42, 45.27, 44.98, 40.56, 40.54, 33.79, 33.46, 33.03, 31.03, 29.63, 29.60, 27.53, 27.30, 20.96, 16.46, 15.86
5k	1694, 1603	2.16–2.30 (m, 1 H), 2.34–2.46 (m, 1 H), 2.64–2.81(m, 1 H), 2.82–2.98 (m, 2 H), 7.10–7.38 (m, 5 H), 12.20–12.40 (br s, 2 H)	175.18, 172.95, 138.77, 128.96, 128.31, 126.34, 42.49, 36.92, 34.85

Table 4 Spectroscopic Data for 3-Alkyl Succinic Anhydrides **6a**–**k**

Product	IR (film) (cm^{-1})	^{1}H NMR (CDCl$_3$) δ (ppm), *J* (Hz)	^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm)	MS: *m/z*
6a	1861, 1784	0.91 (d, 3 H, *J* = 6.4), 0.95 (d, 3 H, *J* = 6.4), 1.43–1.54 (m, 1 H), 1.62–1.76 (m, 1 H), 1.77–1.87 (m, 1 H), 2.56–2.68 (m, 1 H), 2.98–3.18 (m, 2 H)	174.07, 170.18, 40.10, 39.21, 34.58, 26.10, 22.68, 21.43	157 [M$^+$], 141, 113, 100, 84, 56 (100), 43
6b	1860, 1781, 1712	1.56–1.78 (m, 3 H), 1.8–1.97 (m, 1 H), 2.18 (s, 3 H), 2.4–2.57 (m, 2 H), 2.61–2.84 (m, 1 H), 3.01–3.22 (m, 2 H)	208.09, 173.68, 170.13, 42.71, 40.82, 34.17, 30.40, 30.20, 20.77	184 [M$^+$], 166, 156, 141, 112, 58, 43 (100)
6c	1860, 1780	0.91 (d, 6 H, *J* = 6.6), 1.14–1.42 (m, 2 H), 1.48–1.74 (m, 2 H), 1.86–2.05 (m, 1 H), 2.58–2.76 (m, 1 H), 3.0–3.18 (m, 2 H)	173.65, 170.12, 40.77, 35.62, 34.00, 28.83, 27.73, 22.32, 22.20	169, 155, 137, 100, 83, 70, 56 (100), 41, 29
6d	1866, 1790	0.95 (t, 3 H, *J* = 7.3), 1.34–1.48 (m, 2 H), 1.54–1.68 (m, 1 H), 1.83–1.97 (m, 1 H), 2.57–2.7 (m, 1 H), 2.98–3.14 (m, 2 H)	173.67, 170.12, 40.45, 34.08, 32.99, 20.02, 13.54	114, 100, 70 (100), 55, 42, 29
6e	1861, 1783, 1732	1.22–1.41 (m, 6 H), 1.43–1.71 (m, 2 H), 2.02 (s, 3 H), 2.4–2.83 (m, 2 H), 3.01–3.16 (m, 1 H), 4.0 (t, 2 H, *J* = 6.6)	177.52, 173.61, 170.05, 64.32, 40.61, 34.09, 30.85, 28.69, 28.44, 26.58, 25.59, 20.97	224, 199, 181, 164, 43 (100)
6f	1862, 1782	0.9 (t, 3 H, *J* = 6.4), 1.24– 1.48 (m, 6 H), 1.55–1.75 (m, 1 H), 1.85–2.04 (m, 1 H), 2.58–2.76 (m, 1 H), 3.0–3.18 (m, 2 H)	173.61, 170.05, 40.67, 34.08, 31.21, 30.96, 26.36, 22.32, 13.91	152, 142, 100, 98, 83, 70, 56 (100), 55, 41, 29, 27
6g	1864, 1778, 1603	1.87–2.0 (m, 1H), 2.24–2.37 (m, 1H), 2.54–2.88 (m, 3 H), 2.96–3.1 (m, 2 H)	173.66, 170.02, 139.53, 128.81, 128.28, 126.70, 39.76, 34.16, 32.90, 32.53	204 [M$^+$], 186, 132, 105, 104 (100), 100, 91, 77, 55, 39
6h	1859, 1780	0.96–1.32 (m, 6 H), 1.48–1.58 (m, 1 H), 1.60–1.80 (m, 3 H), 1.80–1.93 (m, 1 H), 2.70 (dd, 1 H, *J* = 4.9, 18), 2.86–3.06 (m, 2 H)	173.42, 170.99, 46.81, 39.42, 31.70, 30.63, 28.81, 26.37, 26.19	182 [M$^+$], 164, 137, 110, 100 (100), 81, 67, 55, 41, 27
6i	1860, 1780	0.87 (t, 3 H, *J* = 6.7), 1.16–1.44 (br s, 18 H), 1.54–1.70 (m, 1 H), 1.84–1.98 (m, 1 H), 2.58–2.72 (m, 1 H), 3.02–3.16 (m, 2 H)	173.65, 170.10, 40.67, 34.08, 31.90, 30.99, 29.58, 29.47, 29.32, 29.78, 29.07, 26.70, 22.68, 14.12	254 [M$^+$], 236, 182, 156, 142, 111, 97 (100), 83, 69, 43, 41, 29
6j	1861, 1782	0.94 (d, 1.8 H, *J* = 6.9), 1.03 (d, 1.2 H, *J* = 6.6), 1.4–1.8 (m, 3 H), 2.15 (s, 1.8 H), 2.17 (s, 1.2 H), 2.46–2.58 (m, 2 H), 2.7–3.22 (m, 3 H)	207.85, 207.64, 173.15, 172.54, 170.14, 170.04, 45.87, 45.49, 40.86, 33.78, 33.06, 31.81, 31.74, 30.02, 29.93, 29.75, 27.50, 26.75, 16.38, 14.86	170, 152, 141, 127, 58, 43 (100),
6k	1842, 1764, 1600	2.73 (dd, 1 H, *J* = 6.6, 19.0), 2.89–3.12 (m, 2 H), 3.26 (dd, 1 H, *J* = 5.0, 14.1), 3.38–3.56 (m, 1 H), 7.10–7.48 (m, 5 H)	173.3, 170.02, 136.02, 129.17, 128.94, 127.63, 42.14, 36.02, 32.96,	190 [M$^+$], 172, 162, 148, 117, 91 (100), 77, 51, 39

Table 5 Spectroscopic Data for 2-Alkylidene Succinic Acids **7a**–**e**

Product	IR (film) (cm^{-1})	^{1}H NMR (CDCl$_3$) δ (ppm), *J* (Hz)	^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm)
7a	1828, 1694, 1652	1.09 (d, 6 H, *J* = 6.9), 2.56–2.77 (m, 1 H), 3.52 (s, 2 H,), 6.88 (d, 1 H, *J* = 10.2)	172.00, 168.26, 150.07, 124.48, 32.04, 27.53, 21.78
7b	1713	2.04 (s, 3 H), 2.37–2.49 (m, 2 H), 2.6 (t, 2 H, *J* = 6.9), 3.38 (s, 2 H), 6.98 (t, 1 H, *J* = 7.6)	207.38, 176.06, 171.59, 146.45, 125.63, 31.86, 29.89, 23.09, 20.83
7c	1710	0.92 (d, 6 H, *J* = 6.7), 1.68–1.87 (m, 1 H), 2.01 (dd, 2 H, *J* = 7.0, 7.6), 3.38 (s, 2 H), 7.12 (t, 1 H, *J* = 7.6)	176.93, 172.18, 147.82, 125.13, 38.09, 32.16, 29.70, 28.22, 22.45
7d	1708, 1676	1.0 (t, 3 H, *J* = 7.6), 2.18 (q, 2 H, *J* = 7.5), 3.2 (s, 2 H), 6.98 (t, 1 H, *J* = 7.5), 12.28 (br s, 2 H)	171.94, 168.06, 145.39, 126.09, 31.83, 21.52, 12.91
7e	3344, 1714	1.2–1.47 (m, 6 H), 2.08–2.22 (m, 2 H), 3.18 (s, 2 H), 3.36 (t, 2 H, *J* = 6.4), 6.8 (t, 1H, *J* = 7.5), 12.2 (br s, 2 H)	171.93, 168.01, 144.01, 126.60, 60.52, 32.25, 28.13, 27.90, 25.16, 20.99

Table 6 Spectroscopic Data for *(E)*-3-Alkylidene Succinic Anhydrides **8a**–**e**

Product	IR (film) (cm^{-1})	^{1}H NMR (CDCl$_3$) δ (ppm), *J* (Hz)	^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm)	MS: *m/z*
8a	1844, 1776, 1676	1.12 (d, 6 H, *J* = 6.6), 2.4–2.6 (m, 1 H), 3.53 (d, 2 H, *J* = 2.6), 6.9 (dt, 1 H, *J* = 2.6, 9.9)	168.72, 165.49, 151.98, 120.46, 31.79, 30.71, 21.35	154 [M$^+$], 139, 126, 111, 95, 67 (100), 39
8b	1841, 1778, 1716, 1683	2.2 (s, 3 H), 2.3–2.56 (m, 2 H), 2.72 (dd, 2 H, *J* = 6.2 and 6.6), 3.62 (br s, 2 H), 6.8–6.96 (m, 1H)	206.44, 168.70, 165.15, 143.74, 124.08, 41.03, 32.18, 30.08, 24.65	154, 139, 122, 111, 43 (100)
8c	1706, 1684	1.0 (d, 6 H, *J* = 6.6), 1.78–2.0 (m, 1H), 2.08–2.2 (m, 2 H), 3.46–3.52 (m, 2 H), 7.0–7.16 (m, 1 H)	168.67, 165.06, 145.34, 123.34, 40.00, 38.29, 32.20, 28.26, 22.61	140, 126 (100), 124, 109, 98, 81, 43
8d	1840, 1777, 1680	1.7 (t, 3 H, *J* = 7.5), 2.23 (q, 2 H, *J* = 7.7), 3.48–3.53 (m, 2 H), 6.98–7.08 (m, 1 H)	168.83, 165.24, 147.44, 122.11, 34.66, 24.32, 12.36	140 [M$^+$], 125, 112, 96, 67 (100), 53, 39
8e	1841, 1778, 1732, 1681	1.34 –1.42 (m, 2 H), 1.44–1.77 (m, 4 H), 2.07 (s, 3 H), 2.17–2.33 (m, 2 H), 3.47 (br s, 2 H), 4.04 (t, 2 H, *J* = 6.62), 6.98–7.08 (m, 1 H)	171.21, 168.35, 164.84, 145.48, 122.78, 64.06, 31.88, 30.64, 28.32, 25.68, 21.00	222, 207, 198, 180, 107, 43 (100)

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