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A facile synthesis of alkyl substituted maleic anhydrides: radical approach

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ABSTRACT

Synthetic background for the preparation of alkyl substituted maleic anhydrides and maleimides based on radical alkylation of 2,3-dichloromaleic anhydride (maleimide) by hydrocarbons was developed. The best conditions for the selective synthesis of 2-alkyl-3-chloro- and unsymmetrically substituted dialkylmaleic anhydrides were elaborated.

1. Introduction

Maleic anhydrides and maleimides are essential intermediates for the synthesis of fine chemicals, including natural substances and their analogues.[1] In addition, a number of natural products containing a substituted maleic anhydride unit have been reported in the literature. They are of great interest due to antibacterial, plant growth promoting, immunomodulating activities, and also activity against Lewis lung carcinoma cell lines.[2]

There are several synthetic approaches for the synthesis of alkyl- and dialkylsubstituted maleic anhydrides reported in the literature.[3] On the one hand, ionic chemistry-based synthetic routes generally employ either different organometallic coupling (S_N2/S_N2' coupling of Grignard reagents,[4] Negishi or Suzuki coupling[5]) or copper-mediated tandem vicinal difunctionalization of dimethyl acetylenedicarboxylate.[6]

On the other hand, the target products can be generated in metal-free radical approaches. Firstly, synthesis of substituted maleimides, based on the Barton decarboxylation reaction,[7] should be mentioned. The key phase of the latter method is the three-step functionalization of maleimide (Scheme 1). Radical addition of the thiohydroxamic ester of the appropriate acid **1** gives addition product **2**, and subsequent oxidation of the intermediate, followed by the decomposition of the corresponding sulfone, produces substituted maleimide **3**.

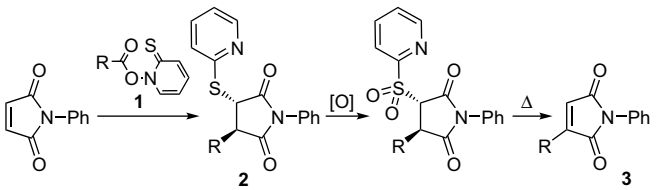
Another intriguing radical approach is a not yet sufficiently developed one-step radical chain addition–elimination reaction with 2,3-dichloromaleic anhydride **4** (Scheme 2).[8]

Taking advantage of the knowledge of 2,3-dichloromaleic anhydride alkylation kinetics,[9] we developed selective, cost-effective and time-efficient preparative methods for substituted maleic anhydrides' synthesis. Synthetic results are summarized in Table 1.

2. Discussion

For our studies we addressed cyclohexane, toluene and 1,4-dioxane as representative examples of different types of 'hydrocarbons', producing correspondingly alkyl, benzylic, and α-alkoxyalkyl radicals. It was found that the rate of the reaction greatly depends on the nature of the 'hydrocarbon' and decreases in the row: alkyl>benzyl>1,4-dioxan-2-yl. We also determined that the rate of substitution of the first chlorine atom is about 30–100 times greater than the rate of the second substitution in **4**. This observation provided us with a background for selective synthesis of 2-alkyl-3-chloromaleic and 2,3-dialkylmaleic anhydrides, and consequently products **6**–**9** were isolated in good yields (60–80%). The reaction with 1,4-dioxane proceeds slowly and some polymerization of the product occurs, therefore **10** was obtained in only 40% yield, and all attempts to obtain 3,4-di-(1,4-dioxan-2-yl) maleic anhydride were unsuccessful.

Owing to the high selectivity of the substitution of the two chlorine atoms in **4**, a one-pot synthesis of unsymmetrically dialkylsubstituted maleic anhydrides seemed feasible. Thus, anhydride **11** was synthesized in 50% yield starting from 2,3-dichloromaleic anhydride. When we attempted to obtain 2-benzyl-3-cyclohexylmaleic anhydride **20**, to our surprise, we observed that the substitution of the alkyl radical competes with the substitution of the second chlorine atom (Scheme 3). In this case, a mixture of products was obtained.



Scheme 1. Synthesis of substituted maleimides based on Barton decarboxylation.

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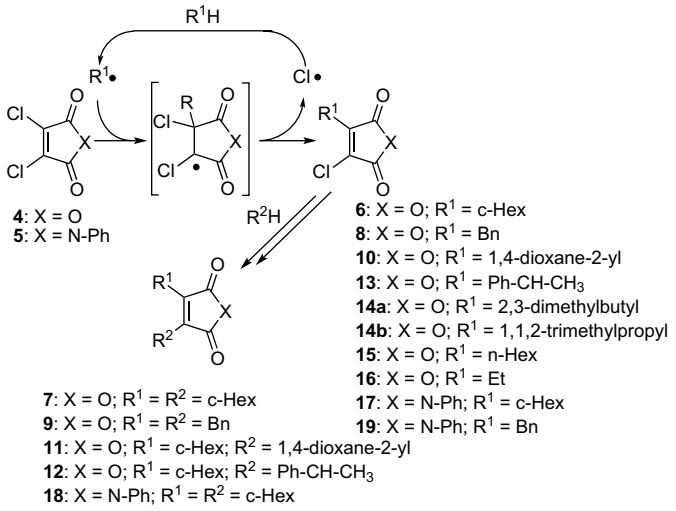
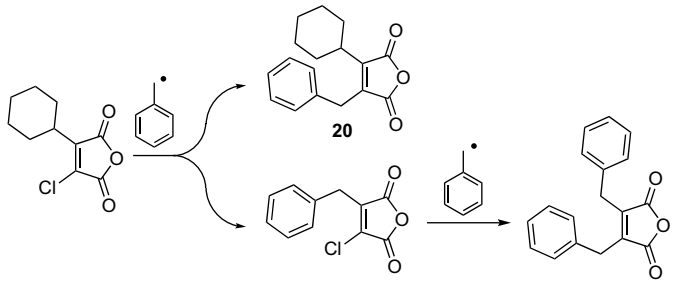


Scheme 2. Synthesis of substituted maleic anhydrides based on radical addition–elimination reaction.

At this point a discrepancy with previous synthesis was raised. There was no side alkyl–alkyl substitution in the preparation of **11**. Therefore, we believe that the steric factor plays a general role in the alkyl radical exchange. To support this hypothesis, we have assumed that the reaction of **6** with more bulky ethylbenzene should proceed without exchange of cyclohexyl substituent, and, indeed, this reaction led to **12** without any side process.

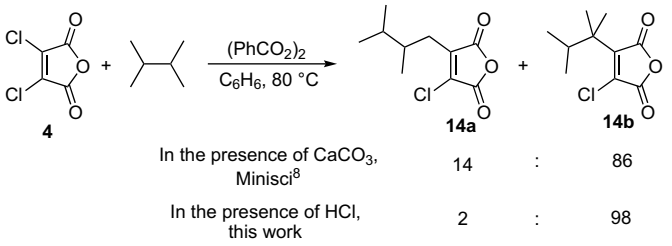
In the chain process of alkylation of 2,3-dichloromaleic anhydride, abstraction of a hydrogen atom from the hydrocarbon proceeds by the chlorine radical. Thus, there is a question of regioselectivity in the case of hydrocarbons with non-equivalent C–H bonds. Some solvents, such as benzene or carbon disulfide, are known to give complexes with a chlorine atom, thus increasing the selectivity of hydrogen abstraction process.[10] Since ethylbenzene is



Scheme 3. Alkyl exchange in radical benzylation of 2-chloro-3-cyclohexylmaleic anhydride.

such a solvent, the reaction of **4** in neat ethylbenzene selectively leads to **13** (quantity of β-isomer is less than 0.1%). However, reaction of **4** in neat 2,3-dimethylbutane results in a mixture of isomers. In our previous kinetic investigations,[9] we found that the reaction regioselectivity is increased with increasing HCl concentration in the reaction medium. Using this fact together with a complexing solvent strategy we improved the reaction selectivity of **4** with 2,3-dimethylbutane up to 2:98 (**14b**/**14a**) (Scheme 4).

We can assert that solvent and HCl effects are powerful instruments to generate selectively the most thermodynamically stable alkyl radical and subsequent alkylation product, but selective



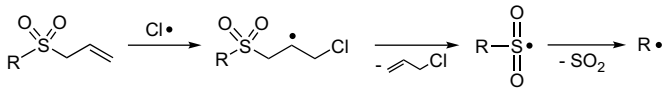
Scheme 4. Reaction of 2,3-dichloromaleic anhydride with 2,3-dimethylbutane.

Table 1
Synthesis of substituted maleic anhydrides

Substrate	Reagent	Product	Method[a]	Yield, %	Properties	Literature yield, % (time, h)
4	Cyclohexane	**6**	A 5%[b] $(PhCO_2)_2$, reflux, 40 min	80	Bp 132–135 °C (2 Torr)	72 (3)[8c] 91 (20)[8b]
4	Cyclohexane	**7**	A 2[c]×[20% $(PhCO_2)_2$, reflux, 3 h]	70	Mp 117–119 °C (from cyclohexane)	76 (100)[8b]
4	Toluene	**8**	A 10% (t-BuO)$_2$, reflux, 2 h	63	Mp 54–55 °C (from hexane)	48 (2)[8c] 47 (54)[8b]
4	Toluene	**9**	A 5×[10% (t-BuO)$_2$, reflux, 2 h]	58	Oil	18 (7 steps)[1b]
4	1,4-Dioxane	**10**	A 3×[5% $(PhCO_2)_2$, 85 °C, 2 h]	40	Mp 98–99 °C (from Et_2O)	35 (3)[8c] 20 (80)[8b]
4	Cyclohexane 1,4-Dioxane	**11**	D	52	Oil	—
6	Ethylbenzene	**12**	A 5×[15% (t-BuO)$_2$, reflux, 2 h]	32	Oil	—
4	Ethylbenzene	**13**	A 20% $(PhCO_2)_2$, 90 °C, 2 h	20	Mp 52–54 °C (from hexane)	—
4	2,3-Dimethylbutane	**14b**	B	78	Oil	15 (2)[8c] (**14a**/**14b**=86:14)
4	n-Hex$SO_2CH_2CH{=}CH_2$	**15**	C	35	Oil	—
4	Et$SO_2CH_2CH{=}CH_2$	**16**	C	33	Oil	—
5	Cyclohexane	**17**	A 10% $(PhCO_2)_2$, reflux, 3 h	70	Mp 89–91 °C (from cyclohexane)	—
5	Cyclohexane	**18**	A 4×[10% $(PhCO_2)_2$, reflux, 3 h]	30	Oil	—
5	Toluene	**19**	A 2×[10% (t-BuO)$_2$, reflux, 2.5 h]	52	Mp 105–107 °C (from hexane)	—

[a] See Section 3.
[b] mol % according to substrate.
[c] Number of repetitions.

generation of the less thermodynamically stable radical from a hydrocarbon is impossible by this method. Therefore, an alternative source of radicals should be used for the preparation of such products. In our work, we also checked the possibility of an application of alkylallylsulfones fragmentation[11] as a method for alkyl radical generation (Scheme 5), and prepared **15** in 35% yield.



Scheme 5. Alkyl radical generation from alkylallylsulfone.

This strategy is also important in the case of introduction of non-bulky alkyl radicals, such as ethyl, to avoid robust direct alkylation with gaseous alkanes (synthesis of **16**). It should be mentioned that the main disadvantage of the alkylallylsulfone approach is moderate yields due to a number of side reactions.

Alkylation strategies discussed in this work can also be applied to maleimides, and, e.g., we synthesized **17**–**19** starting from 2,3-dichloro-*N*-phenylmaleimide. However, delocalization of the nitrogen lone pair to the maleimide ring leads to decreased electrophilicity of the carbon–carbon double bond as compared to maleic anhydride, and thus reaction with maleimides proceeds more slowly. The literature data indicate that the reaction of 2,3-dichloromaleic anhydride with amines selectively gives the corresponding 2,3-dichloromaleimides.[12] Therefore, substituted maleimides are believed to be produced from suitably substituted maleic anhydrides, which were described earlier.

In conclusion, the synthesis of 2-alkyl-3-chloro and 2,3-dialkylmaleic anhydrides by free-radical alkylation of 2,3-dichloromaleic anhydride is simple and cost-efficient. We have developed useful procedures for the selective synthesis of a number of substituted maleic anhydrides. We believe that our methods will be of valuable impact to the investigations in the field of maleic anhydride synthesis.

3. Experimental

3.1. General

Melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured at 300 and 75 MHz, respectively, on a Bruker DPX-300 instrument in $CDCl_3$. Chemical shifts refer to residual $CHCl_3$ on the δ scale. GLC analysis was carried out on Varian-3700 type chromatograph with 30 m capillary column (HP-1). MS were obtained at ionization energy of 70 eV. IR spectra were measured on Shimadzu IRAffinity-1 FTIR spectrophotometer. All solvents were dried and distilled prior to use. 2,3-Dichloromaleic anhydride[13] and 2,3-dichloro-*N*-phenylmaleimide[13] were synthesized and used just after recrystallization. Column chromatography was carried out on silica gel 0.035–0.070 mm (Acros Organics).

3.2. General procedure for the allkylation of 2,3-dichloromaleic anhydride (method A)

A mixture of 2,3-dichloromaleic anhydride[13] (1.0 g, 6.0 mmol) or 2,3-dichloro-*N*-phenylmaleimide[13] (970 mg, 4 mmol), appropriate quantity of initiator and hydrocarbon (10 ml) (Table 1) was heated in a flask equipped with a reflux condenser until all substrates react or no additional product was produced. The progress of the reaction was monitored by GLC. Every 2–3 h an additional portion of initiator was added. For the number of initiator additions and reaction time see Table 1. The product was isolated by column chromatography on silica gel using pure hexane as eluent first and then hexane–1,2-dichloroethane (5:1) mixture. For purifying **18**, pure 1,2-dichloroethane was utilized. Solid products were additionally purified by recrystallization. Compounds **17** and **19** were purified by recrystallization without use of column chromatography.

3.2.1. 2-Chloro-3-cyclohexylmaleic anhydride (*6*)

Colourless oil (1.0 g, 80%); bp 132–135 °C (2 Torr). [Found: C, 56.1; H, 5.2. $C_{10}H_{11}ClO_3$ requires C, 55.94; H, 5.13%] ν_{max} (KBr) 3700–3300 (br), 2935, 2857, 1775, 1634, 1451, 1249, 1065, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.75 (1H, quint, *J* 7.8 Hz, CH), 1.95–1.65 (7H, m, CH_2), 1.45–1.20 (3H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 162.6, 160.4, 147.6, 134.7, 36.7, 29.3, 26.1, 25.7.

3.2.2. 2,3-Dicyclohexylmaleic anhydride (*7*)

Colourless crystals (1.1 g, 70%); mp 117–119 °C (cyclohexane). [Found: C, 73.2; H, 8.5. $C_{16}H_{22}O_3$ requires C, 73.28; H, 8.40%.] δ_H (300 MHz, $CDCl_3$) 2.68 (2H, tt, *J* 3.6, 12.0 Hz, CH), 2.00–1.55 (14H, m, CH_2), 1.45–1.20 (6H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 165.4, 147.4, 36.7, 30.4, 26.4, 25.7.

3.2.3. 2-Benzyl-3-chloromaleic anhydride (*8*)

Off white solid (840 mg, 63%); mp 54–55 °C (hexane). [Found: C, 59.3; H, 3.2. $C_{11}H_7ClO_3$ requires C, 59.33; H, 3.15%.] ν_{max} (KBr) 3700–3300 (br), 1780, 1647, 1496, 1270, 1250, 1037, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.37–7.28 (5H, m, Ph), 3.88 (2H, s, CH_2); δ_C (75 MHz, $CDCl_3$) 163.1, 160.2, 142.9, 136.3, 134.2, 129.7, 129.5, 128.3, 30.9.

3.2.4. 2,3-Dibenzylmaleic anhydride (*9*)

Colourless thick oil (970 mg, 58%). [Found: C, 77.3; H, 5.3. $C_{18}H_{14}O_3$ requires C, 77.70; H, 5.04%.] ν_{max} (KBr) 3700–3300 (br), 3030, 1860, 1822, 1764, 1454, 1274, 1193, 1082, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.36–7.27 (6H, m, Ph), 7.17 (4H, dd, *J* 2.1, 7.5 Hz, Ph), 3.83 (4H, s, CH_2); δ_C (75 MHz, $CDCl_3$) 166.2, 143.4, 135.4, 129.5, 129.3, 127.9, 30.7.

3.2.5. 2-Chloro-3-(1,4-dioxane-2-yl)-maleic anhydride (*10*)

Pale yellow solid (520 mg, 40%); mp 98–99 °C (Et_2O). [Found: C, 43.6; H, 3.4. $C_8H_7ClO_5$ requires C, 43.94; H, 3.20%.] ν_{max} (KBr) 3700–2700 (br), 1785, 1732, 1629, 1350–1200 (br), 1103 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.77 (1H, dd, *J* 3.0, 9.6 Hz, CH), 3.97–3.72 (6H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 161.3, 159.6, 139.3, 138.3, 70.6, 67.7, 67.1, 66.6; *m*/*z* (EI, 70 eV) 220 (12 M$^+$), 218 (26, M$^+$), 190 (43), 188 (100), 146 (17), 144 (37), 116 (51), 87 (43%).

3.2.6. 2-Cyclohexyl-3-(1-phenylethyl)-maleic anhydride (*12*)

Colourless thick oil (540 mg, 32%). [Found: C, 75.7; H, 7.2. $C_{18}H_{20}O_3$ requires C, 76.06; H, 7.04%.] ν_{max} (KBr) 3700–3300 (br), 2937, 2856, 1844, 1765, 1648, 1453, 1257, 1123, 1025, 961, 907 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.40–7.27 (5H, m, Ph), 4.28 (1H, q, *J* 7.5 Hz, PhC*H*), 2.64 (1H, tt, *J* 3.3, 11.7 Hz, $CH^{c\text{-}Hex}$), 1.88–1.68 (7H, m, CH_2), 1.71 (3H, d, *J* 7.5 Hz, CH_3), 1.38–1.22 (3H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 165.3, 165.0, 147.9, 146.2, 140.9, 129.3, 127.79, 127.76, 36.9, 36.0, 30.1, 30.0, 26.4, 26.3, 25.7, 18.2.

3.2.7. 2-Chloro-3-(1-phenylethyl)-maleic anhydride (*13*)

White solid (280 mg, 20%); mp 52–54 °C (hexane). [Found: C, 61.2; H, 3.8. $C_{12}H_9ClO_3$ requires C, 60.89; H, 3.81%.] ν_{max} (KBr) 3700–3300 (br), 2940, 1861, 1794, 1636, 1497, 1448, 1382, 1274, 1241, 1093, 975, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.41–7.36 (5H, m, Ph), 4.30 (1H, q, *J* 7.2 Hz, CH), 1.79 (3H, d, *J* 7.2 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 162.4, 160.2, 146.2, 139.5, 135.2, 129.5, 128.4, 128.0, 37.2, 17.4.

*3.2.8. 2-Chloro-3-cyclohexyl-N-phenylmaleimide (**17**)*

Pale yellow solid (810 mg, 70%); mp 89–91 °C (cyclohexane). [Found: C, 66.2; H, 5.4; N, 4.7. $C_{16}H_{16}ClNO_2$ requires C, 66.32; H, 5.53; N, 4.84%.] ν_{max} (KBr) 3700–3300 (br), 3066, 2950–2800 (br), 1800–1550 (br), 1506, 1401, 1201, 1140, 1118, 943 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.53–7.33 (5H, m, Ph), 2.84 (1H, tt, *J* 3.9, 11.4 Hz, CH), 1.95–1.73 (7H, m, CH_2), 1.43–1.31 (3H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 168.0, 164.7, 144.3, 132.8, 131.7, 129.5, 128.4, 126.3, 36.2, 29.8, 26.5, 25.9; *m*/*z* (EI, 70 eV) 291 (32 M^+), 289 (100 M^+), 254 (50), 236 (10), 234 (28), 223 (40), 221 (100), 77 (60%).

*3.2.9. 2,3-Dicyclohexyl-N-phenylmaleimide (**18**)*

Pale yellow thick oil (400 mg, 30%). [Found: C, 78.1; H, 7.7; N, 4.3. $C_{22}H_{27}NO_2$ requires C, 78.34; H, 8.01; N, 4.15%.] ν_{max} (KBr) 3700–3300 (br), 2928, 2853, 1707, 1600, 1501, 1450, 1384, 1116 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.55–7.34 (5H, m, Ph), 2.77 (2H, tt, *J* 3.5, 12.0 Hz, CH), 1.98–1.62 (14H, m, CH_2), 1.42–1.27 (6H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 170.5, 144.1, 134.2, 130.6, 129.2, 126.3, 36.6, 31.0, 26.8, 26.1.

*3.2.10. 2-Benzyl-3-chloro-N-phenylmaleimide (**19**)*

Yellow solid (620 mg, 52%); mp 105–107 °C (hexane). [Found: C, 68.4; H, 4.1; N, 4.5. $C_{17}H_{12}ClNO_2$ requires C, 68.57; H, 4.03; N, 4.71%.] ν_{max} (KBr) 3700–3300 (br), 1720, 1651, 1598, 1493, 1383, 1113 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.53–7.27 (10H, m, Ph), 3.92 (2H, s, CH_2); δ_C (75 MHz, $CDCl_3$) 168.0, 164.5, 139.8, 135.7, 134.5, 131.6, 129.62, 129.58, 129.4, 128.5, 127.8, 126.3, 30.4.

3.3. 2-Chloro-3-(1,1,2-trimethylpropyl)-maleic anhydride (14b) (method B)

A mixture of 2,3-dichloromaleic anhydride (500 mg, 3 mmol), benzoyl peroxide (150 mg, 0.6 mmol), 2,3-dimethylbutane (2 ml), an acetonitrile solution of HCl ([HCl]=2.7 M, 2 ml) and benzene (6 ml) was heated for 2 h at 80 °C in a sealed tube. An additional portion of benzoyl peroxide (75 mg, 0.3 mmol) was added, and the mixture was heated for 1 h more. The progress of the reaction was monitored by GLC. The product was isolated by column chromatography analogous to method A. Removal of the solvent gave **14b** (510 mg, 78%) as a colourless oil with 97% purity (GLC). [Found: C, 55.1; H, 5.8. $C_{10}H_{13}ClO_3$ requires C, 55.43; H, 6.00%.] ν_{max} (KBr) 3700–3300 (br), 2968, 1836, 1775, 1610, 1467, 1250, 1139, 930 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.34 (1H, sept, *J* 6.9 Hz, C*H*Me_2), 1.40 (6H, s, CMe_2), 0.88 (6H, d, *J* 6.9 Hz, CHMe_2); δ_C (75 MHz, $CDCl_3$) 162.4, 160.6, 149.5, 135.2, 42.3, 34.9, 22.9, 17.9.

3.4. Alkylallylsulphones as the source of radicals (method C)

A mixture of 2,3-dichloromaleic anhydride (1 g, 6 mmol), corresponding alkylallylsulphone (3 mmol), *tert*-butyl peroxide (60 mg, 0.4 mmol) and chlorobenzene (10 ml) was refluxed in a flask equipped with a reflux condenser for 2 h. An additional alkylallylsulphone (1.5 mmol) and *tert*-butyl peroxide (60 mg, 0.4 mmol) were added and reflux was continued for additional 2 h. The last operation was repeated once more. Products were isolated by column chromatography as described in method A.

*3.4.1. 2-Chloro-3-hexylmaleic anhydride (**15**)*

Colourless oil (450 mg, 35%). [Found: C, 55.5; H, 6.1. $C_{10}H_{13}ClO_3$ requires C, 55.43; H, 6.00%.] ν_{max} (KBr) 3700–3300 (br), 2938, 1770, 1642, 1352, 1255, 1084, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.58 (2H, t, *J* 7.5 Hz, C=C–CH_2), 1.66 (2H, quint, *J* 7.5 Hz, C=C–CH_2CH_2), 1.43–1.28 (6H, m, CH_2), 0.91 (3H, t, *J* 6.5 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 163.2, 160.2, 145.0, 136.2, 31.6, 29.4, 27.1, 25.1, 22.8, 14.3.

*3.4.2. 2-Chloro-3-ethylmaleic anhydride (**16**)*

Colourless oil (320 mg, 33%). [Found: C, 45.2; H, 3.4. $C_6H_5ClO_3$ requires C, 44.86; H, 3.12%.] ν_{max} (KBr) 3700–3300 (br), 1795, 1284, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.61 (2H, q, *J* 7.5 Hz, CH_2), 1.27 (3H, t, *J* 7.5 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 163.0, 160.3, 145.8, 135.9, 18.7, 11.4.

3.5. One-pot synthesis of 2-cyclohexyl-3-(1,4-dioxan-2-yl)-maleic anhydride (11) (method D)

A mixture of 2,3-dichloromaleic anhydride (0.5 g, 3 mmol) and benzoyl peroxide (15 mg, 0.06 mmol) was heated in a flask equipped with a reflux condenser for 1.5 h. The solvent was removed under reduced pressure and 1,4-dioxane (10 ml) was added. An additional benzoyl peroxide (70 mg, 0.3 mmol) was added and mixture was heated to reflux for 1 h. This operation was repeated six times. Product was isolated by column chromatography as described in method A to give **11** (420 mg, 52%) as a viscous yellowish oil. [Found: C, 62.8; H, 6.5. $C_{14}H_{22}O_5$ requires C, 63.16; H, 6.77%.] ν_{max} (KBr) 3700–2700 (br), 1800–1700 (br), 1630, 1400–1200 (br), 1082, 927 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.73 (1H, dd, *J* 3.0, 10.2 Hz, CH^{diox}); 3.89–3.70 (5H, m, CH_2^{diox}), 3.57 (1H, dd, *J* 10.2, 11.4 Hz, O–CH_aH_eCH–O), 3.11 (1H, tt, *J* 3.6, 11.7 Hz, $CH^{c\text{-}Hex}$), 1.92–1.58 (7H, m, $CH_2^{c\text{-}Hex}$), 1.36–1.22 (3H, m, $CH_2^{c\text{-}Hex}$); δ_C (75 MHz, $CDCl_3$) 164.5, 164.4, 152.5, 137.7, 71.6, 69.4, 67.3, 66.7, 37.0, 30.6, 30.3, 26.4, 26.3, 25.7; *m*/*z* (EI, 70 eV) 266 (93 M^+), 238 (20), 236 (20), 222 (26), 204 (100), 176 (60), 134 (73%).

References and notes

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