Smooth Generation of 3*H*-2-Benzopyran-3-ones and their Diels–Alder Reactions with Olefinic Dienophiles

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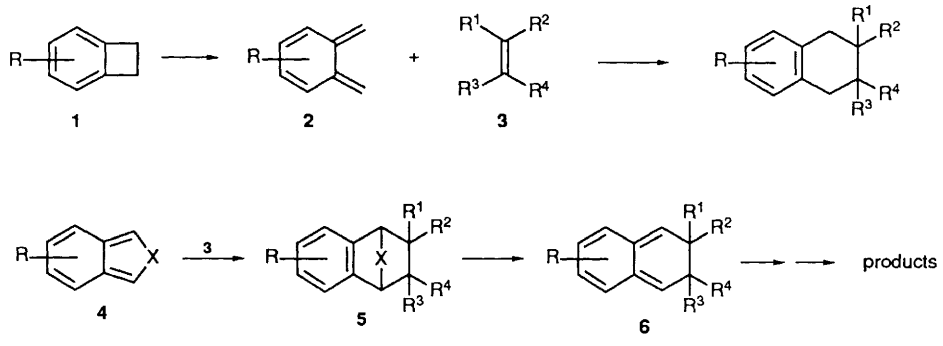
The generation of methoxy-substituted 3*H*-2-benzopyran-3-ones from *o*-acylphenylacetic acid derivatives in acetic anhydride at 140 °C and their *in situ* Diels–Alder reactions being inefficient in the synthesis of some carbocyclic compounds, alternative reagents have been used. It is shown that, *e.g.* 1,3-dicyclohexylcarbodiimide (DCC) with 2-hydroxypyridine, disuccinimidyl carbonate (DSC), 2-ethoxy-*N*-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) of 2-isobutoxy-*N*-isobutoxycarbonyl-1,2-dihydroquinoline (IIDQ) are much more efficient reagents.

Using these alternative reagents the formation of side-products from the benzopyranone, *e.g.* chrysene, can be avoided; with the modified DCC-method the 6,7-dimethoxy-1-methyl-2-benzopyran-3-one intermediate **8a** can be identified spectroscopically. An exemplified procedure with IIDQ is proposed, opening new prespectives for Diels–Alder reactions of unstable or less reactive dienophiles with problematic benzopyranones.

In recent years *ortho*-quinodimethane systems have proved to be very useful in intramolecular[1] as well as in intermolecular[2] Diels–Alder reactions with various dienophiles. *ortho*-Quinodimethane systems of type **2** can be generated by thermolysis of benzocyclobutenes **1** and can be brought into reaction with, *e.g.*, olefinic dienophiles **3** (Scheme 1).[3]



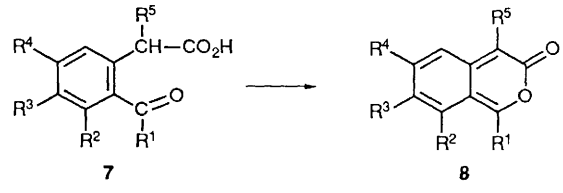
Scheme 1

In an alternative approach, *ortho*-quinodimethane systems of type **6** can be obtained by extrusion of X from adducts **5**, prepared *via* a Diels–Alder reaction of compounds **4** with dienophiles **3**. According to literature data, X can be CO,[4] –N=N–,[5] S,[6] O,[7], NH[8] and –CO·O–.[9] The latter lactone precursor type has been used mainly by Jones and co-workers.[9] By heating *o*-acylphenylacetic acid derivatives **7** in acetic anhydride they generated 3*H*-2-benzopyran-3-ones **8** *in situ* (Scheme 2). During our work on some benzopyranones and their addition reactions, we observed that this procedure did not give satisfactory results in a number of cases. We therefore started a search for methods enabling us to generate and attempt to cause to react specifically substituted benzopyranones (compounds **8a–c**) under more convenient conditions.

Results and Discussion

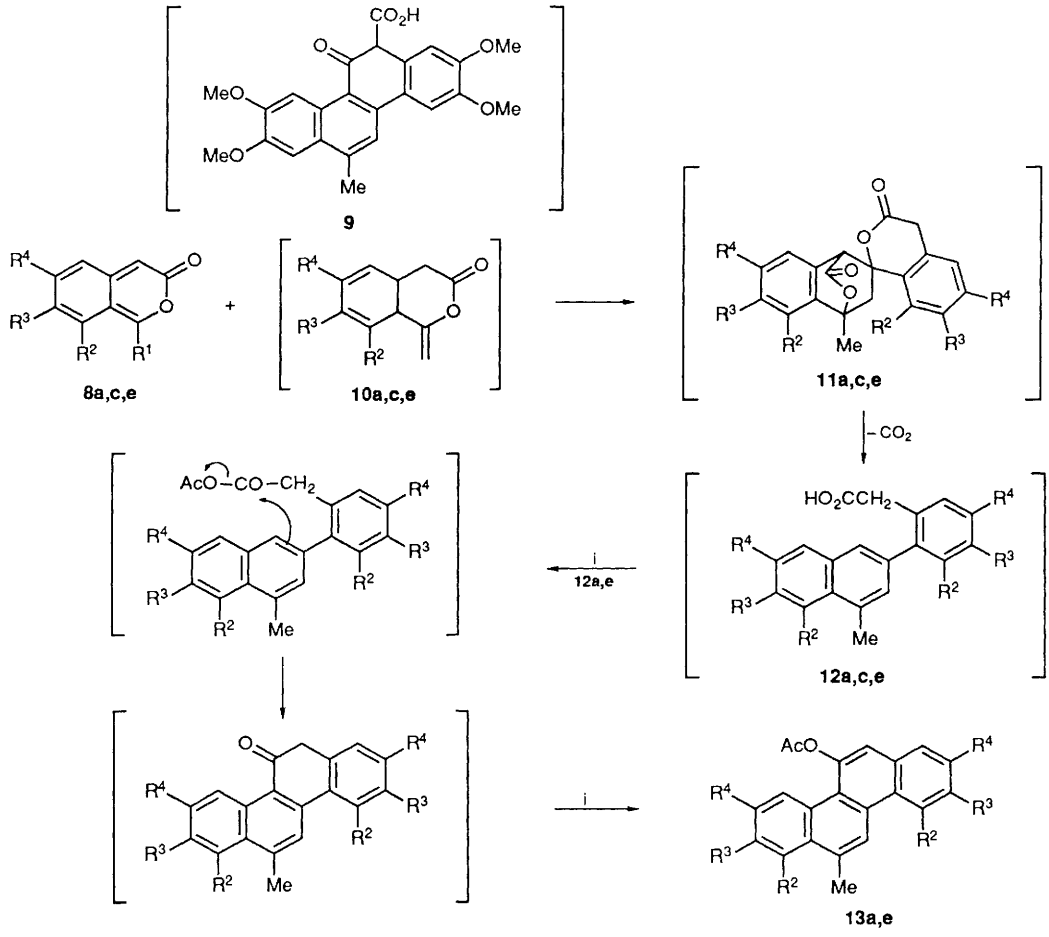
The drastic conditions used to generate benzopyranones (*T* 140 °C, Ac_2O) generally do not allow one to isolate them. Moreover, this procedure brought about side-reactions when benzopyranones with R^1 = H were used or when attempts were made to trap them with less reactive or unstable dienophiles. With methoxy-substituted benzopyranones, decomposition and loss of CO_2 from the adducts was observed. Furthermore, in the reaction of methoxy-substituted *o*-acetylphenylacetic acid **7a** with poorly reactive dienophiles we isolated a high yield of the chrysene **13a**. Based on the observation[10] that compound **7e** also gave a considerable yield of the corresponding chrysene **13e**, we believe that its formation occurs *via* the pathway outlined in Scheme 3 and probably not *via* an intermediate of type **9**, such as that proposed by Elliot and Evans.[11]

Indeed, if R^1 = Me an intermolecular Diels–Alder reaction can take place between the benzopyranone **8** and its tautomer **10**, yielding spiro compound **11**. An intermediate **11c** of that type was isolated and thermolysed at 260 °C by Jones[12] to yield the intermediate acid **12c** (Scheme 3).



a; R^1 = Me, R^2 = R^5 = H, R^3 = R^4 = OMe
b; R^1 = R^3 = R^5 = H, R^2 = R^4 = OMe
c; R^1 = Me, R^2 = R^3 = R^4 = R^5 = H
d; R^1 = R^2 = R^5 = H, R^3 = R^4 = OMe
e; R^1 = Me, R^2 = R^4 = OMe, R^3 = R^5 = H

Scheme 2 **8f** and **8g** are described in the text



Scheme 3 *Reagent:* i, Ac_2O

Table 1 ^{1}H NMR data (δ) of the benzopyranone **8a**[a]

δ	Coupling and integration	Assignment	δ	Coupling	Assignment	Δ[b]
2.60	d, *J* 1.2, 3 H	1-Me	5.97	m, 1 H	4-H	−0.03
3.88	s, 3 H	7-OMe	6.23	s, 1 H	5-H	0.60
3.94	s, 3 H	6-OMe	6.35	br s, 1 H	8-H	0.60

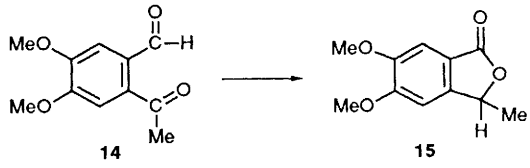
[a] 250 MHz; solvent $CDCl_3$; standard Me_4Si. [b] Δ = δ($CDCl_3$) − δ(C_6D_6).

In the literature there is some evidence that alkoxy substituents accelerate the decarboxylation of both isochroman-3-ones and benzopyranone adducts.[13] This can explain why intermediates **11a** and **11e** were not isolated. Furthermore, owing to the methoxy-substitution pattern a fast cyclisation of compounds **12a** and **12e** activated by Ac_2O can be envisaged.

In order to avoid these side-reactions and to maintain a valuable lactone function, we investigated the generation and reactions of compounds **8a–d** under gentle conditions (20–80 °C). Reactions were used that find common acceptance in peptide chemistry;[14] *e.g.* 1,3-dicyclohexylcarbodiimide (DCC), 2-ethoxy-*N*-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ), 2-isobutoxy-*N*-isobutoxycarbonyl-1,2-dihydroquinoline (IIDQ), disuccinimidyl carbonate (DSC).

Using the DCC method with substrate **7a** at 20 °C in the absence of dienophiles we observed the formation of a yellow product. After careful chromatography (SiO_2) of the reaction mixture we obtained a fraction containing the benzopyranone **8a**, which was spectroscopically characterised. Until now, isolation of benzo[*b*]pyranones could only be achieved with the more stable analogues **8f** ($R^1 = R^5$ = Ph, $R^2 = R^3 = R^4$ = H) and **8g** [R^1 = 3,4,5-$(MeO)_3C_6H_2$, $R^2 = R^5$ = H, $R^3R^4 = OCH_2O$].[15] The ^{1}H NMR characteristics of the yellow compound **8a** [λ_{max}(MeOH) 437 nm] are given in Table 1.

Owing to the aromatic-solvent-induced shift (ASIS) in deuteriobenzene (Δδ −0.03 ppm), the absorption at δ 5.97 was assigned to 4-H. The absorption at δ 6.35 was assigned to the 8-H atom on the grounds of its long-range coupling (br s) with the 4-H atom. The δ-values for 4-, 5- and 8-H indicate the non-aromatic character of the benzopyranone system. In solution, the benzopyranone **8a** was quasi-stable at −30 °C. At room temperature it reacted slowly with oxygen to form compound **14**, similar to the product observed by Smith *et al.*[16] in the oxidation of 1,4-diphenyl-2-benzopyran-3-one. Product **14** was observed partly to rearrange into compound **15**, which was isolated.



In order to obtain some idea about the efficacy of our synthetic method we compared the yields of the isolated adducts from reaction of benzopyranones **8a–c** and *N*-phenylmaleimide (NPM). The cyclodehydratation of 2-acetyl-4,5-dimethoxyphenylacetic acid **7a** and 2-formyl-3,5-dimethoxyphenylacetic acid **7b** by the acetic anhydride method in the presence of NPM (5 mol equiv.) did not lead to the isolation of the expected benzopyranone–NPM adducts (**16a** and **b**). These intermediate

Table 2 Product distribution (%) in the reaction of benzopyranones **8a–c** with NPM using different synthetic methods

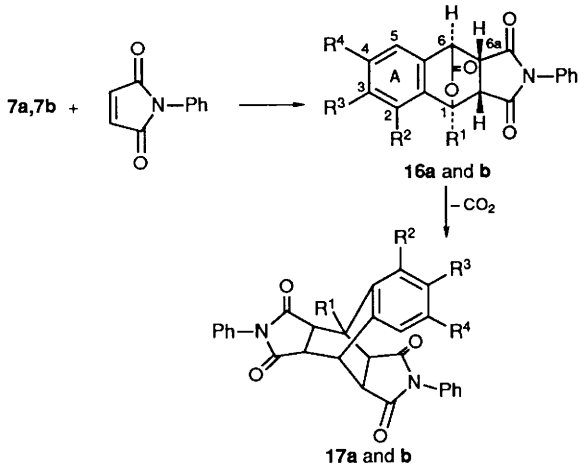
Method	Product				
	16a	**17a**	**16b**	**17b**	**16c**[a]
Ac_2O		89		95	81[b]
DCC/2-hydroxypyridine	97		98		50
DSC	91		85		61
EEDQ, IIDQ	92		83		98

[a] **16c**: R^1 = Me, R^2 = R^3 = R^4 = H. [b] Ref. 18.

Table 3 Yield (%) of products **26–31** in the reaction of compounds **7a** and **7d** with dienophiles **22–25**

Method	Product			
	26–27	**28**	**29–30**	**31**
Ac_2O	41	0	32	0
IIDQ	83	49	62	85

adducts lost CO_2 to yield an *ortho*-quinodimethane system, which was trapped with a second equivalent of NPM to yield compounds **17a** and **17b** (Scheme 4).

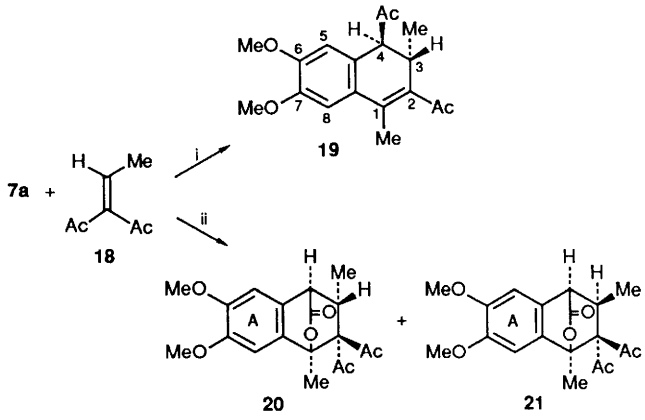


Scheme 4 Non-systematic numbering scheme

Use of DCC as the reagent in benzene with the acid **7a** led to Diels–Alder adduct **16a** but only in low yield (29%). A condensation product (58%) resulting from an intramolecular rearrangement of the intermediate *ortho*-acyl isourea derivative was observed. As in peptide chemistry,[17] this rearrangement could be suppressed by using the catalytic additive 2-hydroxypyridine and by changing the solvent from benzene to acetonitrile.[17b] With this modified DCC-method, a yield increase from 29 to 98% for the previous reaction was established. From the results shown in Table 2, it appears that the DSC-, EEDQ-, IIDQ-methods also give high yields of adducts **16a–c** with NPM as dienophile. However, the IIDQ-method seems to be better for compound **16c** (Table 2).

The configuration of the adducts was deduced from their NMR spectra. The *endo*-configuration was assigned to adducts **16a–c** based on the shielding effect of the aromatic ring A on the *ortho*-protons of the *N*-phenyl group and from the coupling constant of 6-H and 6a-H (J 3.5 Hz). In the case of the *exo*-adduct, the coupling constant would be smaller.[19]

The efficacy of the IIDQ-method was further confirmed by the reaction of acid **7a** with another dienophile compound **18**. With the acetic anhydride method, the latter (Scheme 5) gave only a rearranged product (compound **19**). This probably results from a 1,5-acetyl migration in the intermediate *ortho*-quinodimethane system formed by decarboxylation of the expected adduct. The stereochemistry of compound **19** was deduced from its ^{1}H NMR spectrum. The small coupling constant (J 2 Hz) between 3-H and 4-H can be explained assuming a *trans*-configuration with a pseudo-axial position for 3-Me and a dihedral angle of *ca.* 90°.



Scheme 5 *Reagents:* i, Ac_2O; ii, IIDQ. Non-systematic numbering scheme

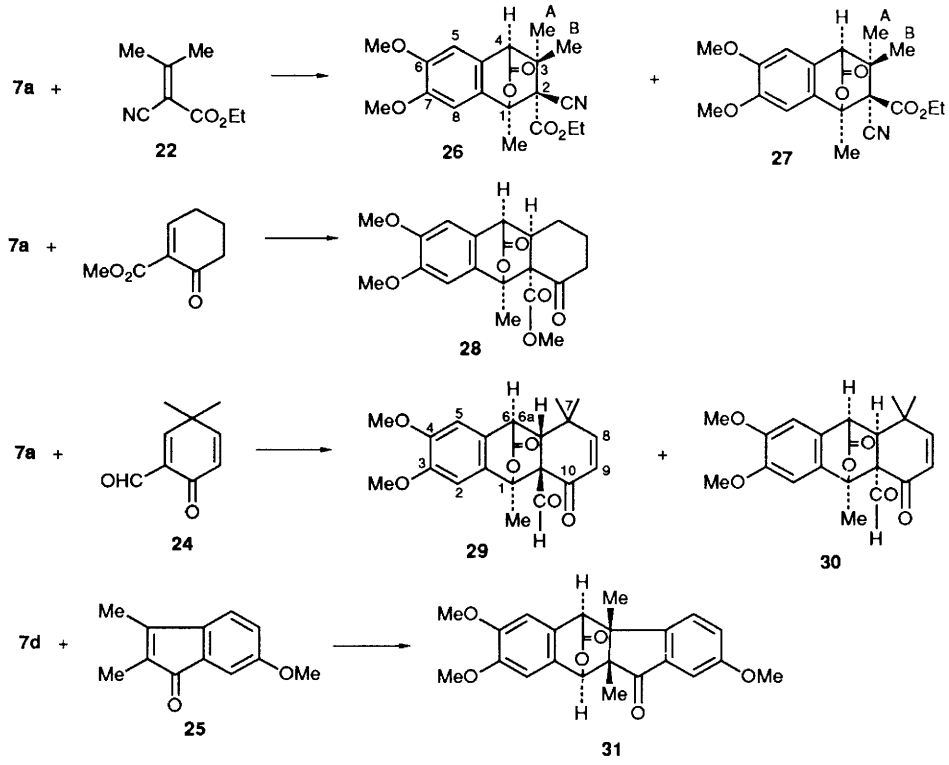
When the DCC/2-hydroxypyridine or DSC-method was used, no adducts at all, or only a low yield of adducts **20** and **21**, could be isolated. With IIDQ (1.2 mol equiv.) in acetonitrile at 60 °C, a 92% yield of the adducts was obtained. The configuration of the adducts **20** and **21** was deduced from the shielding effect of the aromatic ring A on 3-Me in product **20** (δ 0.70; δ 1.40 in **21**) and on 3-H in product **21** (δ 2.74; δ 3.44 in **20**). The above mentioned IIDQ reagent was shown to be very efficient in the generation and reaction of the benzopyranone **8a** with less reactive or unstable dienophiles (*e.g.* compounds 22–24). It was also efficient in the reaction of the benzopyranone **8d** with the 2,3-dimethylindenone **25**. With the acetic anhydride method only a low or no yield of adducts **26–31** (Scheme 6 and Table 3) was obtained.

The proposed regiochemistry in compounds **28–30** is in agreement with the coupling between 6-H and 6a-H (J 2.1). The same regiochemistry is assumed for adducts **26** and **27** because the position and solvent shift for the 1-Me and the 4-H NMR signals in both compounds are comparable with those of compounds **28–30**. The regiochemistry of adduct **31** is assumed to be the same as in similar adducts described in a previous paper.[20]

The *endo*-configuration of compound **29** was assigned on the grounds of the shielding effect of the aromatic ring on 8-H and 9-H. Owing to the similarity of the signals of 6a-H in *exo*-structure **30** and in **28** (respectively δ 2.72 and 2.78) we assume an *exo*-structure for compound **28**. The 6a-H signal is shifted to lower field (δ 3.35) in compound **29**.

Distinction between compounds **26** and **27** was made by consideration of the ^{1}H NMR signals of Me^A and Me^B. They appear much closer to each other in compound **26** (Me^A: δ 1.19; Me^B: δ 1.34) than in compound **27** (Me^A: δ 0.75; Me^B: δ 1.68). This is interpreted in terms of four different anisotropic effects:[21] shielding (+) from the ester function and lactone bridge, a more pronounced shielding effect from the benzene ring (++) and deshielding from the nitrile group (−). The assignment of the *endo*-structure for adduct **31** is based on the highfield absorption of the aromatic protons (δ 6.37–7.4) and the aromatic methoxy group[20] (δ 3.60).

Conclusions.—The acetic anhydride method for the generation of benzopyranones from *o*-acylphenylacetic acids and for



Scheme 6 Non-systematic numbering schemes

trapping them with dienophiles was shown to be inefficient in some cases. This is due to, *e.g.*, the formation of chrysene by-products or decomposition of the primary adduct. This was avoided by the use of alternative reagents. IIDQ in particular allowed the isolation of Diels–Alder adducts of problematic benzopyranones with some uncommon dienophiles, which could not be used with the acetic anhydride method. The thermolysis of some of these adducts is under current investigation.

Experimental

IR spectra were recorded as thin films between NaCl plates or as solids in KBr pellets on a Perkin-Elmer 297 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 250 MHz and 62.5 MHz, respectively. *J*-Values are given in Hz. Mass spectra were recorded on a Kratos MS 50 instrument operating at 70 eV and 150–250 °C as required. Exact mass measurements were performed at a resolution 10 000. MN-Kieselgel 60 (230–400 Mesh) and chloroform stabilised with amylene were used for chromatographic separations. All solvents and reagents were dried and purified by standard procedures. All cycloadditions were performed under nitrogen or *in vacuo*. Phenylacetic acids **7a–d**,[11,22] dienophiles **18**,[23] **22**,[24] **23**,[25] **24**[26] and **25**[27] were prepared as previously described.

Generation of the 6,7-*Dimethoxy*-1-*methyl*-2-*benzopyran*-3-*one* **8a** *by the DCC-Method.*—A solution of the phenylacetic acid **7a** (0.21 g, 0.9 mmol), DCC (0.172 g, 0.9 mmol) and 2-hydroxypyridine 0.112 g, 1.2 mmol) in dry acetonitrile (6 cm^3) was stirred under nitrogen for 2 h at 25 °C. After removal of the solvent under reduced pressure the residue was chromatographed on silica gel (fast column) with 90% $CHCl_3$–10% EtOAc (maintaining a nitrogen atmosphere during all operations). A yellow fraction was concentrated under nitrogen and afforded the spectroscopically identified title compound **8a**, ν_{max}(NaCl)/cm^{-1} 1750 (CO); δ_C(62.5 MHz; $CDCl_3$; Me_4Si) 17.9 (q, 1-Me), 55.7 (q, 6-OMe), 56.2 (q, 7-OMe), 99.6 (2 × br d, J_{CH} 168, C-4), 100.0 (2 × s, J_{CH} 160, C-8), 100.7 (dd, J_{CH} 162, C-5), 111.8 (m, C-8a), 146.5 (d, C-4a), 148.4 (m, C-7 or -6), 157.3 (m, C-6 or -7), 161.5 (m, C-1) and 162.3 (d, CO); *m*/*z* 220 (M$^+$, 52%), 192 (100), 177 (17) and 149 (34).

Decomposition of the Benzopyranone **8a**: *Formation of* 2-*Acetyl*-4,5-*dimethoxybenzaldehyde* **14** *and* 5,6-*Dimethoxy*-3-*methyl*-3H-*isobenzofuran*-1-*one* **15**.—A solution of the benzopyranone **8a** in $CHCl_3$ was exposed for 24 h to air and light. TLC and NMR analysis of the evaporated mixture indicated the formation of two compounds. Column chromatography (SiO_2; 5% EtOAc–95% $CHCl_3$ as eluent) gave a fraction containing a pure component to which the structure of compound **15** was assigned, based on the NMR data shown below. For the other compound, which decomposed on the column, structure **14** was proposed.

For *compound* **14**: δ_H(250 MHz; $CDCl_3$) 2.64 (3 H, s), 3.99 (3 H, s), 4.01 (3 H, s), 7.17 (1 H, s), 7.45 (1 H, s) and 10.2 (1 H, s).

For *compound* **15** (Found: M$^+$, 208.0734. $C_{11}H_{12}O_4$ requires M, 208.0736); ν_{max}(NaCl)/cm^{-1} 1720–1750 (CO); δ_H[250 MHz; $CDCl_3$: $\Delta = \delta(CDCl_3) - \delta(C_6D_6)$ ppm] 1.62 (3 H, d, *J* 7, Δ 0.46), 3.94 (3 H, s, Δ 0.70), 4.00 (3 H, s, Δ 0.72), 5.46 (1 H, q, *J* 7, Δ 0.52), 6.83 (1 H, s, Δ 0.66) and 7.27 (1 H, s, Δ 0.10); *m*/*z* 208 (M$^+$, 48%), 193 (54) and 165 (100).

Trapping of Benzopyranones **8a–c** *with NPM: Synthesis of the Benzopyranone–NPM Adducts* **16a–c**.—(a) *With DCC and* 2-*hydroxypyridine in acetonitrile: general procedure.* A mixture of a phenylacetic acid **7a–c** (0.200 g, *ca.* 0.9 mmol), DCC (1 mmol) and 2-hydroxypyridine (1.2 mmol) in dry acetonitrile (5 cm^3) was stirred under nitrogen for 2 h at 25 °C (yellow colour of benzopyranone appeared). Then, a solution of NPM (10 mmol) in dry MeCN (5 cm^3) was added dropwise to the mixture, the solution was stirred at room temperature for 16 h and then evaporated under reduced pressure and the residue was

chromatographed on silica gel with gradient elution (100% $CHCl_3$ to 5% EtOAc–95% $CHCl_3$) to give adducts **16a–c**, which were crystallised from MeOH.

For *compound* **16a** (0.32 g, 97%); m.p. 206–207 °C (Found: M^+, 393.1209. $C_{22}H_{19}NO_6$ requires M, 393.1212); ν_{max}(KBr)/cm^{-1} 1720 and 1770 (CO); δ_H(250 MHz; $CDCl_3$) 2.22 (3 H, s), 3.64 (1 H, d, *J* 8.5), 3.71 (1 H, dd, *J* 8.5 and 3.5), 3.88 (3 H, s), 3.90 (3 H, s), 4.38 (1 H, d, *J* 3.5), 6.55 (2 H, m), 6.86 (1 H, s), 6.89 (1 H, s) and 7.31 (3 H, m); *m/z* 393 (M^+, 45%), 349 (45), 220 (57) and 202 (100).

For *compound* **16b** (0.33 g, 98%); m.p. 161–163 °C (Found: M^+, 379.1056. $C_{21}H_{17}NO_6$ requires M, 379.1058); ν_{max}(KBr)/cm^{-1} 1725 and 1770 (CO); δ_H(250 MHz; $CDCl_3$) 3.66 (1 H, dd, *J* 8.5 and 3.2), 3.80 (6 H, s), 3.96 (1 H, dd, *J* 8.5 and 4.5), 4.39 (1 H, d, *J* 3.8), 6.37 (1 H, d, *J* 4.5), 6.44 (1 H, d, *J* 2.4), 6.50 (1 H, d, *J* 2.4), 6.60 (2 H, m) and 7.33 (3 H, m); *m/z* 379 (M^+, 10%) 335 (1), 224 (100), 143 (100) and 99 (100).

For *compound* **16c** (0.19 g, 50%); m.p. 150 °C (Found: M^+, 333.1000. $C_{20}H_{15}NO_4$ requires M, 333.1001); ν_{max}(KBr)/cm^{-1} 1720 and 1770 (CO); δ_H (250 MHz; $CDCl_3$) 2.24 (3 H, s), 3.60 (1 H, d, *J* 8), 3.69 (1 H, dd, *J* 8 and 3.5), 4.45 (1 H, d, *J* 3.5), 6.45 (2 H, m), 7.27 (3 H, m) and 7.41 (4 H, m); *m/z* 333 (M^+, 17%), 289 (23), 233 (13) and 142 (100).

On performing the reaction of the aldehyde **7a** with DCC in benzene (5 cm^3) without 2-hydroxypyridine, compound **16a** was formed in low yield (0.095 g, 29%) together with an *o*-acyl isourea derivative (0.22 g, 58%).

(b) *The DSC-method: general procedure.* A mixture of a phenylacetic acid **7a–c** (0.2 g, *ca.* 0.9 mmol), DSC (1.2 mmol), dry triethylamine (1 mmol) and NPM (5 mmol) in dry acetonitrile (5 cm^3) was stirred under nitrogen for 24 h at room temperature. After work-up as prescribed above the adducts **16a–c** were obtained in 91, 85 and 61% yield, respectively.

(c) *The IIDQ- or EEDQ-method: general procedure.* A solution of a phenylacetic acid **7a–c** (0.2, *ca.* 0.9 mmol), EEDQ or IIDQ (1.2 mmol) and NPM (3 mmol) in dry acetonitrile (10 cm^3) was heated at 50 °C under nitrogen for 24 h and then evaporated under reduced pressure; the residue was dissolved in $CHCl_3$ (200 cm^3). The solution was extracted successively three times with 1 mol dm^{-3} HCl (3 × 30 cm^3) saturated aq. $NaHCO_3$ and water. The chloroform layer was dried on $MgSO_4$, then evaporated under reduced pressure and the residue was purified by column chromatography on silica gel with 5% EtOAc–95% $CHCl_3$ as eluent. The yield of each adduct (**16a–c**) was, respectively, 92, 83 and 98%.

(d) *Acetic anhydride method: generation of bis-adducts* **17a** *and* **17b**. The phenylacetic acid **7a** (0.23 g, 1 mmol) or the phenylacetic acid **7b** (0.4 g, 1.8 mmol), NPM (5 mmol for **7a**, 10 mmol for **7b** and acetic anhydride (6 cm^3; freshly distilled from quinoline) were refluxed for 16 h under nitrogen. Excess of acetic anhydride was evaporated off under reduced pressure. The residue was chromatographed (SiO_2) with 95% $CHCl_3$–5% EtOAc and afforded compound **17a** or **17b**, which was recrystallised from methanol.

For *compound* **17a** (0.47 g, 89%); m.p. >240 °C (Found: M^+, 522.1858. $C_{31}H_{26}N_2O_6$ requires M, 522.1858); ν_{max}(KBr)/cm^{-1} 1717 and 1775 (CO); δ_H(250 MHz; $CDCl_3$) 2.15 (3 H, s), 2.94 (2 H, d, *J* 9), 3.27 (2 H, dd, *J* 9 and 3), 3.80 (6 H, s), 4.12 (1 H, t, *J* 3), 6.60 (4 H, m), 6.78 (1 H, s), 6.80 (1 H, s) and 7.30 (6 H, m); *m/z* 522 (M^+, 100%), 349 (43) and 200 (67).

For *compound* **17b** (0.86 g, 95%); m.p. >240 °C (Found: M^+, 508.1627. $C_{30}H_{24}N_2O_6$ requires M, 508.1634); ν_{max}(KBr)/cm^{-1} 1720 and 1770 (CO); δ_H(250 MHz; $CDCl_3$) 3.32 (4 H, br s), 3.74 (3 H, s), 3.75 (3 H, s), 4.18 (1 H, br s), 4.74 (1 H, br s), 6.43 (2 H, m), 6.65 (4 H, m) and 7.31 (6 H, m); *m/z* 508 (M^+, 100%), 335 (12) and 188 (75).

Trapping of the Benzopyranone **8a** *with Dienophile* **18**.—Ac_2O-*Method: generation of* 2,4-*diacetyl*-6,7-*dimethoxy*-1,3-*dimethyl*-3,4-*dihydronaphthalene** **19**. A mixture of compound **7a** (0.4 g, 1.7 mmol), dienophile **18** (1 g, 8 mmol) and acetic anhydride (20 cm^3; freshly distilled from quinoline) were refluxed for 3 h under nitrogen. The mixture was evaporated under reduced pressure and the residue was chromatographed (SiO_2; 95% $CHCl_3$–5% EtOAc) to give the *decarboxylated product* **19** (0.43 g, 85%) (Found: M^+, 302.1515. $C_{18}H_{22}O_4$ requires M, 302.1518); ν_{max}(KBr)/cm^{-1} 1610 (C=C) and 1670 (CO); δ_H(250 MHz; $CDCl_3$) 1.00 (3 H, d, *J* 7), 2.01 (3 H, s), 2.20 (3 H, s), 2.42 (3 H, s), 3.30 (1 H, d, *J* 2), 3.34 (1 H, qd, *J* 2 and 7), 3.90 (3 H, s), 3.92 (3 H, s), 6.77 (1 H, s) and 6.95 (1 H, s); *m/z* 302 (M^+, 13%), 259 (28), 217 (99) and 202 (100).

IIDQ-method: generation of adducts **20** *and* **21**. A mixture of compound **7a** (0.2 g, 0.9 mmol), IIDQ (1.2 mmol) and dienophile **18** (5 mmol) in dry acetonitrile (3 cm^3) was degassed by subsequent freeze-pump-thaw cycles and was then heated in a sealed tube for *ca.* 18 h at 80 °C. After evaporation of solvent and excess of dienophile, followed by usual work-up and chromatography (SiO_2: 95% $CHCl_3$–5% EtOAc) as for compounds **16a–c**, the adducts **20** and **21** were obtained.

For *compounds* **20** and **21** (0.27 g, 92%) (ratio 60:40) (Found: M^+, 346.1419. $C_{19}H_{22}O_6$ requires M, 346.1416); ν_{max}(KBr)/cm^{-1} 1700–1720 (CO); for **20**: δ_H(250 MHz; $CDCl_3$) 0.70 (3 H, d, *J* 7), 1.87–2.33 (9 H), 3.44 (1 H, qd, *J* 3 and 7), 3.70 (1 H, d, *J* 3), 3.89 (6 H, s), 6.79 (1 H, s) and 7.10 (1 H, s); for adduct **21**: δ_H 1.40 (3 H, d, *J* 7), 1.87–2.33 (9 H), 2.74 (1 H, qd, *J* 2 and 7), 3.74 (1 H, d, *J* 2), 3.90 (6 H, s), 6.75 (1 H, s) and 6.79 (1 H, s); *m/z* 346 (M^+, 7%), 220 (62) and 192 (100).

Trapping of compounds **7a** *and* **7d** *with Dienophiles* **22–25**.—IIDQ-method: synthesis of compounds **26–32**, *general procedure.* A mixture of an acid **7a** or **7d** (0.2 g, *ca.* 0.9 mmol), IIDQ (1.2 mmol), and dienophile **23** (5 mmol), **22** and **24** (10 mmol), or **25** (2 mmol) in dry acetonitrile (3 cm^3) was allowed to react, worked up and chromatographed as described for the reaction with dienophile **18**. Adducts **27–32** were obtained as single products or as mixture of isomers.

Products **26** and **27** (0.26 g, 83%) were obtained as a 1:1 mixture which could be partially separated by HPLC.

Compound **26** (Found: M^+, 373.1519. $C_{20}H_{23}NO_6$ requires M, 373.1525); ν_{max}(NaCl)/cm^{-1} 1750–1770 (CO) and 2220 (CN); δ_H(250 MHz; $CDCl_3$) 1.19 (3 H, s), 1.34 (3 H, s), 1.39 (3 H, t, *J* 7), 2.12 (3 H, s), 3.46 (1 H, s), 3.92 (3 H, s), 3.93 (3 H, s), 4.37 (2 H, q, *J* 7), 6.82 (1 H, s) and 6.93 (1 H, s); *m/z* 373 (M^+, 14%) and 220 (100).

For compound **27**; ν_{max}(NaCl)/cm^{-1} 1750–1770 (CO) and 2220 (CN); δ_H(250 MHz; $CDCl_3$) 0.75 (3 H, s), 1.27 (3 H, t, *J* 7), 1.68 (3 H, s), 2.12 (3 H, s), 3.43 (1 H, s), 3.89 (3 H, s), 3.94 (3 H, s), 4.16 (2 H, q, *J* 7), 6.74 (1 H, s) and 7.00 (1 H, s); *m/z* 373 (M^+, 14%) and 220 (100).

Compound **28** was a yellow oil (0.15 g, 49%) (Found: M^+, 374.1358. $C_{20}H_{22}O_7$ requires M, 374.1365); ν_{max}(NaCl/cm^{-1} 1705 (CO), 1720 (CO_2Me) and 1750 (CO lactone); δ_H(250 MHz; $CDCl_3$) 1.86 (2 H, m), 2.11 (3 H, s), 2.19 (2 H, m), 2.59 (2 H, m), 2.78 (1 H, m), 3.55 (3 H, s), 3.75 (1 H, d, *J* 2.1), 3.90 (3 H, s), 3.92 (3 H, s), 6.78 (1 H, s) and 6.97 (1 H, s); *m/z* 374 (M^+, 14%), 330 (7), 220 (80) and 192 (100).

For *compounds* **29** and **30** (0.19 g, 62%) (ratio 1:3) (Found: M^+, 370.1407. $C_{21}H_{22}O_6$ requires M, 370.1416); ν_{max}(NaCl)/cm^{-1} 1665 (CO), 1725 (CHO) and 1765 (CO).

For compound **29**; δ_H(250 MHz; $CDCl_3$) 0.96 (3 H, s), 1.34 (3 H, s), 2.11 (3 H, s), 3.35 (1 H, t, *J* 2), 3.89 (6 H, s), 4.10 (1 H, d, *J* 2),

* *Systematic name*: 1,3-diacetyl-6,7-dimethoxy-2,4-dimethyl-1,2-dihydronaphthalene.

5.24 (1 H, d, *J* 10), 6.16 (1 H, dd, *J* 10 and 2 Hz), 6.64 (1 H, s), 6.78 (1 H, s) and 10.32 (1 H, s).

For compound **30**; δ_H(250 MHz; $CDCl_3$) 1.00 (3 H, s), 1.46 (3 H, s), 2.05 (3 H, s), 2.72 (1 H, t, *J* 2), 3.89 (3 H, s), 3.92 (3 H, s), 4.06 (1 H, d, *J* 2), 6.20 (1 H, d, *J* 10), 6.71 (1 H, dd, *J* 10 and 2), 6.77 (1 H, s), 6.88 (1 H, s) and 10.00 (1 H, s); *m/z* 370 (M^+, 8%) and 220 (100).

For *compound* **31** (0.25 g, 85%); m.p. 179–181 °C (Found: M^+, 394.1419. $C_{23}H_{22}O_6$ requires M, 394.1416); ν_{max}(KBr)/cm^{-1} 1700 and 1745 (CO); δ_H (250 MHz; $CDCl_3$) 1.52 (3 H, s), 1.58 (3 H, s), 3.63 (3 H, s), 3.70 (3 H, s), 3.77 (3 H, s), 3.97 (1 H, s), 5.37 (1 H, s), 6.37 (1 H, s), 6.75 (1 H, s), 6.77 (1 H, d, *J* 3), 7.14 (1 H, dd, *J* 3 and 8) and 7.42 (1 H, d, *J* 8); *m/z* 394 (M^+, 10%), 206 (100) and 178 (28).

With the Ac_2O-method with dienophiles **22**–**25**, the chrysene **13a** [11] was observed when using substrate **7a** and low yields (30–40%) of compounds **26** and **27**, or **29** and **30**, or no yield at all [for adducts **28** and **31**] were obtained.

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