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PHOTOCHEMICAL REACTIONS OF 6-METHOXYBENZOFURAN-2,3-DIONE WITH STYRENE AND β-ETHOXYSTYRENE

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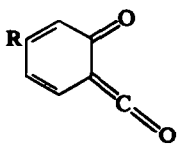
Abstract—Irradiation of a benzene solution of 6-methoxybenzofuran-2,3-dione containing excess styrene or β-ethoxystyrene gives a yellow crystalline product which has been identified as 6-methoxyisoaurone by comparison with an authentic sample.

Considerable interest has recently been aroused by the generation of the keto-ketene (**1a**) by irradiation of various precursors, including benzofuran-2,3-dione (**2a**).[1-5] The keto-ketene has been observed spectroscopically and has also been trapped by nucleophilic reagents. Of particular interest is the generation of the keto-ketene from flavanone (**3**),[6] since a similar fragmentation process is of major importance in the mass spectra of flavonoids.[7] We have investigated the possibility of generating the OMe-substituted keto-ketene (**1b**), by irradiation of 6-methoxybenzofuran-2,3-dione (**2b**), in the hope of trapping it by cycloaddition to various alkenes and alkynes. Such a reaction would afford a new general route to benzopyrone derivatives.



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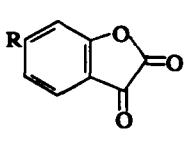
b, R = OMe



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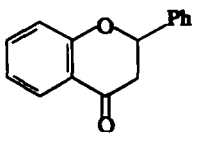

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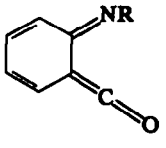

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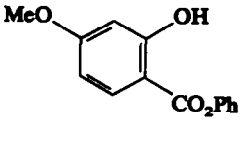

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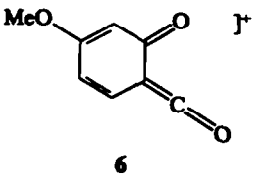

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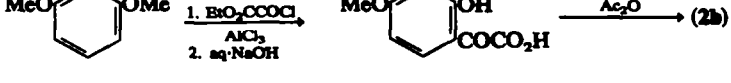
Kametani has recently reported a "retro mass spectral synthesis" of several quinazolones which may involve cycloaddition to the iminoketene (**4**, R = H or Me),[8] and De Mayo has generated the same iminoketene by flash themolysis of some anthranilic acid derivatives.[9]

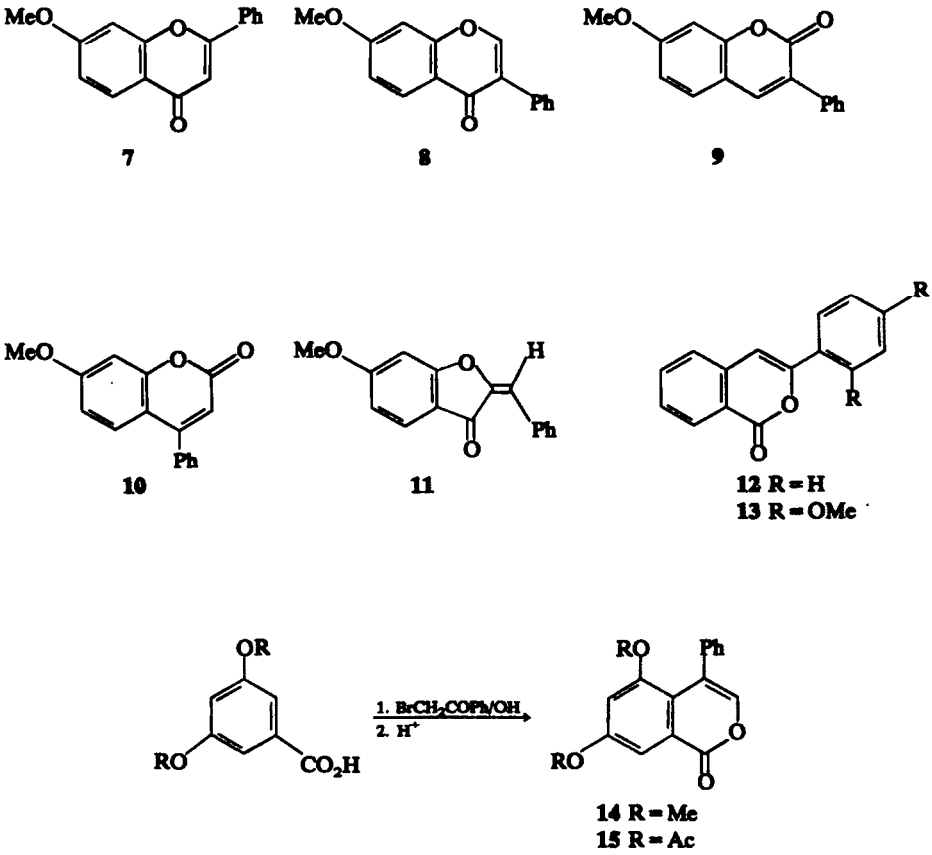
6-Methoxybenzofuran-2,3-dione (**2b**) was prepared by acylation of 1,3-dimethoxybenzene by ethyl oxalylchloride, followed by hydrolysis of the ester, and lactonisation of the glyoxylic acid so formed (Scheme 1). Irradiation of a benzene solution of **2b** containing excess phenol using either a 125 W or a 500 W medium pressure mercury lamp gave phenyl 2-hydroxy-4-methoxybenzoate (**5**) as a major product. This could have been formed by nucleophilic addition to the keto-ketene (**1b**).

Irradiation of a benzene solution of **2b** containing excess β-ethoxystyrene for 3 hrs gave a complex mixture of products from which a yellow crystalline compound (**A**) was isolated in 20% yield. Repeating the same reaction for 30 mins gave a lower yield of **A**, while repeating the reaction for 6 mins resulted in loss of the initial yellow colour of the dione but gave only a very low yield of **A**. To our surprise, **A** was also obtained in 7% yield when styrene was used in place of the β-ethoxystyrene. From the latter reaction a white crystalline product (**B**) of unknown structure was also isolated in 5% yield.

The compound **A**, m.p. 113.5–5°, gave a molecular ion at *m/e* 252.0786 ($C_{16}H_{12}O_3$) and also gave fragment ions at *m/e* 237 and 209, corresponding



Scheme 1



Scheme 2

to loss of Me and CO from the molecular ion. However the mass spectrum showed no peak at *m/e* 150, corresponding to **6**, which would be expected to be a major fragment if **A** were a benzopyrone derivative.[7] Thus **A** has a molecular weight 46 (C_2H_6O) less than would be expected for an adduct of **1b** with β-ethoxystyrene, and 2 (H_2) less than would be expected for an adduct of **1b** with styrene.

Compound **A** had an IR CO stretching frequency of 1770 cm^{-1}, which showed that it could not be the flavone (**7**)[10] or isoflavone (**8**)[11] (Table 1). The IR spectrum also excluded the 3- and 4-phenylcoumarins (**9**[12] and **10**),[13] and the 6-methoxyaurone (**11**),[14] authentic samples of which were available for comparison. The possibility of the compound being a 3- or 4-phenylisocoumarin was ruled out by comparison of the IR spectra (Table 1) and ^{13}C nmr spectra (see below) with those of model compounds (**12–15**). The 3-arylisocoumarins (**12**[15] and **13**)[16] were prepared by standard methods from homophthallic acid. The 4-phenylisocoumarins (**14** and **15**) were prepared by a modification of the method described by Usgaonkar and Desai[17] for the preparation of 4-methylisocoumarins (Scheme 2).

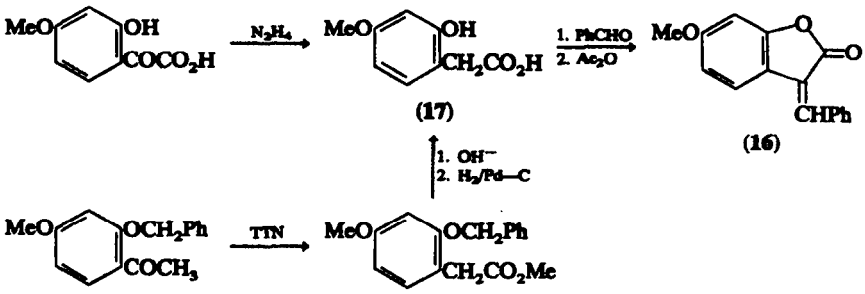
The ^1H NMR spectrum of **A** indicated the presence of a OMe group and also nine aromatic or olefinic protons. Spin decoupling experiments suggested that one aromatic ring was trisubstituted, as in the parent benzofurandione (**2b**), whilst the other aromatic ring (derived from the styrene) was probably monosubstituted.

The compound **A** was inert to aqueous acid but soluble in alcoholic or aqueous base, which suggested the presence of an ester group. However treatment with aqueous base followed by methylation with diazomethane gave a complex mixture from which no pure products could be isolated. Similarly reduction with LAH gave a mixture of products.

Finally, 6-methoxyisoaurone (**16**) was considered as a possible structure for **A**. An authentic sample of the isoaurone was prepared by condensing 2-hydroxy-4-methoxyphenylacetic acid (**17**) with benzaldehyde followed by lactonisation.[18] The required

Table 1. Comparison of m.p., IR and UV data

Compound	m.p.	$\nu_{C=O}$	λ_{max}
7	110–111°	1658	251, 306
8	156°	1665	249, 297
9	125.5–7°	1713	240, 340
10	111–113°	1736	233, 327
11	147°	1694	230, 282, 337
12	90–91°	1720	233, 296, 310, 337
13	169–171°	1727	228, 297, 320, 350
14	123–4°	1714	233, 285, 350
15	165–167°	1737	229, 270, 330
Unknown (**A**)	114–115°	1770	216, 239, 260, 370



Scheme 3

phenylacetic acid (**17**) could be prepared either by Wolff–Kishner reduction[19] of the corresponding glyoxylic acid, or by oxidative rearrangement of 2-benzyloxy-4-methoxyacetophenone using thallium (III) nitrate[20] (Scheme 3). The IR and NMR spectra of the isoaurone (**16**) were superimposable on those of the unknown **A** and its identity was confirmed by mixed mp determination.

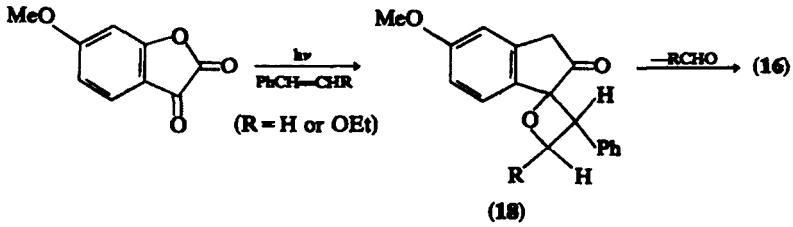
Comparison of the ^{13}C NMR spectra of the various compounds involved in this study was also useful in arriving at the correct structure for **A**. Full details of the ^{13}C spectra are published elsewhere.[21] However one aspect of the spectra which was particularly useful was the observation that the chemical shifts of the central three C atoms are very characteristic of the type of compound present (Table 2). Thus the CO carbon comes at 160 ppm in the coumarins and isocoumarins, 175–7 ppm in the flavone and isoflavone, 183 ppm in the aurone, and 170 ppm in the isoaurone.

It is possible that the formation of the isoaurone (**16**) in the photochemical reactions of **2b** with styrene and β-ethoxystyrene could involve the rearrangement of an initially formed adduct of the keto-ketene (**1b**). However it seems more likely that it arises by cycloaddition of the styrene onto the 3-CO group of the benzofurandione to give an oxetane (**18**, R = H or OEt) which then undergoes elimination of CH_2O or HCO_2Et to give the isoaurone (Scheme 4). In support of this scheme, Friedricksen has recently shown that photolysis of 4,6-dimethylbenzofuran-2,3-dione in the presence of various alkenes gives spirooxetanes similar to **18**.[22]

Table 2. ^{13}C NMR shifts of central three carbon unit[a]

Flavone	**7**	162.6 s (C-2)	107.2 d (C-3)	177.4 s (C=O)
Isoflavone	**8**	125.1 s (C-3)	152.4 d (C-2)	175.3 s (C=O)
Coumarins	**9**	124.7 s (C-3)	139.8 d (C-4)	160.5 s (C=O)
	10	155.8 s (C-4)	111.7 d (C-3)	160.9 s (C=O)
Aurone	**11**	147.7 s (C-2)	111.6 d (=CH)	182.7 s (C=O)
Isocoumarins	**12**	153.4 s (C-3)	101.7 d (C-4)	162.0 s (C=O)
	13	150.6 s (C-3)	99.0 d (C-4)	162.6 s (C=O)
	15	118.7 s (C-4)	140.3 d (C-3)	161.9 s (C=O)
Isoaurone	**16**	122.3 s (C-3)	137.8 d (=CH)	169.8 s (C=O)

[a] multiplicity in off-resonance spectra also indicated; chemical shifts given as p.p.m. downfield of TMS.



Scheme 4

EXPERIMENTAL

IR and UV spectra were recorded using Perkin-Elmer 257 and 402 spectrophotometers respectively. Mass spectra were obtained using an AE1 MS9 double-focussing spectrometer, and ^1H and ^{13}C NMR spectra were obtained using Varian HA-100 and XL-100 instruments, the latter being coupled to a 620L-100 computer. Benzene, used as solvent in the photochemical experiments, was dried by distillation from sodium or LAH. Mallinckrodt standard grade silicic acid was used for column chromatography.

2-Hydroxy-4-methoxyphenylglyoxylic acid. Powdered $AlCl_3$ (27 g) was added at 0° to a mixture of 1,3-dimethoxybenzene (13.8 g) and ethyloxalyl chloride (13.6 g) in 1,2-dichloroethane (150 ml). The mixture was refluxed for 1 hr, cooled, and poured into acidified ice-water. The organic layer was separated, dried, and evaporated under reduced pressure. The residue was warmed with 8% NaOH (50 ml) for 30 min, cooled, acidified and extracted with CH_2Cl_2. The organic extract was dried, evaporated under reduced pressure, and the residue recrystallised from water to give the glyoxylic acid (7.0g, 36%), m.p. 121° (lit.[23] 120–2°).

6-Methoxybenzofuran-2,3-dione (**2b**). The above glyoxylic acid (0.3 g) in Ac_2O (1 ml) was heated under reflux for 5 min. The soln was concentrated and cooled to 0° when yellow crystals separated and were recrystallised from benzene-petroleum ether to give the benzofurandione (0.2 g, 73%), m.p. 135° (lit.[23] 135–6°). $\nu_{C=O}^{KBr}$ 1810, 1730 cm^{-1}. The benzofurandione could also be prepared by refluxing the glyoxylic acid (0.4 g) in benzene (15 ml) with P_2O_5 (3.2 g). The hot soln was filtered, concentrated under reduced pressure, and the benzofurandione (0.15 g, 55%) precipitated by addition of petroleum ether.

Photochemical reactions of 6-methoxybenzofuran-2,3-dione

(a) *With phenol.* 6-Methoxybenzofuran-2,3-dione (0.1 g) and phenol (0.15 g) were dissolved in benzene (100 ml) and, with N_2 continuously passing through, the soln was irradiated with a 125 W medium pressure lamp for 24 hr. The solvent was evaporated under reduced pressure and the residue chromatographed on silica to yield **5** (0.05 g, 36%), m.p. 52–4°, identical with an authentic sample. The same product was also formed when the reactants were irradiated with a 500 W lamp for 2 hr.

(b) *With β-ethoxystyrene.* 6-Methoxybenzofuran-2,3-dione (89 mg) and β-ethoxystyrene[24] (148 mg) were dissolved in benzene (380 ml) and, with N_2 continuously passing through, the soln was irradiated with a 500 W medium pressure lamp for 3 hr. The solvent was evaporated under reduced pressure and the residue subjected to chromatography on silicic acid, eluting initially with CH_2Cl_2 petroleum ether (1:2). The first fraction was found to contain phenyl acetaldehyde, produced by hydrolysis of β-ethoxystyrene. The second fraction afforded the 6-methoxyisaurone (compound **A**) as yellow crystals (25 mg, 20%), m.p. 113.5–115°. $\nu_{C=O}^{KBr}$ 1770 cm^{-1} λ_{max}^{EtOH} 216(3.81), 239(3.79), 260(3.82) and 370(3.85) nm. $\tau(CDCl_3)$ 2.3–2.7 m (7H), 3.35 d (1H, J = 2), 3.4–3.6 dd (1H, J = 2 and 8), 6.23 s (3H). (Found: C, 75.71%; H, 4.92%. $C_{16}H_{12}O_3$ requires: C, 76.18%; H, 4.79%) M^+252.0786. $C_{16}H_{12}O_3$ requires 252.0786). *m/e* 252(100), 237(6), 210(10), 209(55), 152(17). Accurate mass measurements: *m/e* 237.0552 ($C_{15}H_9O_3$), 209.0603 ($C_{14}H_9O_2$). Other fractions from the column were shown by tlc to be complex mixtures of products, but the final fraction, eluted with ethyl acetate, gave 2-hydroxy-4-methoxybenzoic acid (10 mg, 12%), identical with an authentic sample.

(c) *With styrene.* 6-Methoxybenzofuran-2,3-dione (1 g) and styrene (11 ml) were dissolved in benzene (380 ml) and the soln irradiated with a 500 W medium pressure mercury lamp for 75 min. The solvent was evaporated under reduced pressure and the residue chromatographed on silicic acid. This afforded three products, the first being compound **A** (103 mg, 7%), m.p. 114–5°, identical to the product of reaction (b). The other two products were obtained from later fractions and were separated by treatment with $NaHCO_3$ aq. They were 2-hydroxy-4-methoxybenzoic acid (150 mg, 16%) and a white, crystalline, bicarbonate-insoluble, product (compound **B**) (80 mg, 5%), m.p. 182–4°, which was recrystallised from toluene-petroleum ether. ν_{Nujol} 3260 and 1723 cm^{-1}. λ_{max}^{EtOH} 221, 268 and 330 (sh) nm. $\lambda_{max}^{EtOH+NaOH}$ 230 and 272 nm. $\lambda_{max}^{EtOH+AlCl_3}$ 217, 271 and 330 (sh) nm. $\tau(CDCl_3)$ 1.7 br (1H, D_2O exch.), 2.98 d (1H, J = 9), 3.46d (1H, J = 2), 3.57 dd (1H, J = 2 and 9), 2.71 s (5H), 4.81 s (2H), 6.26 s (3H). *m/e* 282(100), 281(13), 251(5), 238(7), 237(28), 225(22), 205(8), 197(22), 177(17), 165(18), 163(14), 152(12), 151(21), 149(12), 105(12), 104(11). (Found M^+ 282.0891. $C_{17}H_{14}O_4$ requires: 282.0891). Accurate mass measurements: *m/e* 251.0708 ($C_{16}H_{11}O_3$), 237.0915 ($C_{16}H_{13}O_2$), 225.0916 ($C_{15}H_{13}O_2$), 197.0965 ($C_{14}H_{13}O$), 177.0552 ($C_{10}H_9O_3$), 149.0603 ($C_9H_9O_2$), 105.0340 (C_7H_5O). ^{13}C NMR ($CDCl_3$ + 1 drop DMSO). 55.10 (q), 70.58 (t), 102.13 (d), 105.62 (d), 110.24 (s), 123.21 (s), 126.92 (d), 128.47(d), 130.20 (d), 131.14 (s), 131.14 (d), 156.07 (s), 161.07 (s), 174.21 (s).

3-Phenylisocoumarin (**12**). A mixture of homophthallic anhydride (6 g), benzene (80 ml) and powdered $AlCl_3$ (7 g) was refluxed for 3 hr. The soln was then cooled and poured into acidified ice-water. The organic layer was separated and extracted with $NaHCO_3$aq. The bicarbonate extract was acidified and the white ppt filtered off and dried to yield 2-carboxydeoxybenzoin (5.8 g). The deoxybenzoin (2g) was dissolved in 85% H_2SO_4 (20 ml) and left to stand for 3 hr. The soln was then poured into ice-water, when a white ppt was obtained which was washed repeatedly with $NaHCO_3$aq and dried to give 3-phenylisocoumarin (0.6 g), m.p. 90–1° (Lit.[15] 90°). $\nu_{C=O}$1720 cm^{-1}. λ_{max}^{EtOH} 233, 296, 310 and 337 nm. $\tau(CDCl_3)$ 1.7–2.8 m (9H), 3.14 s (1H).

3-(2,4-Dimethoxyphenyl)isocoumarin (**13**). 1,3-Dimethoxybenzene (13.8 g) and homophthalic acid (18.0 g) were mixed with polyphosphoric acid (100 g) and the mixture heated on a water-bath at 100° with stirring for 10 min. The brown soln was then poured into cold water and the solid which separated filtered off and recrystallised from glacial ArOH to yield **13** as a white crystalline solid (7.0 g) m.p. 169–171° (Lit.[16] 171°). $\nu_{C=O}$ 1727 cm^{-1}. λ_{max}^{EtOH} 228, 297, 320 and 350 nm. τ(DMSO) 1.8–3.4 m (8H), 6.11 s (3H), 6.19 s (3H).

5,7-Dimethoxy-4-phenylisocoumarin (**14**). 3,5-Dimethoxybenzoic acid (9.1 g) was dissolved in water (75 ml) and the pH adjusted to 6.5 by addition of 5% NaOHaq. Phenacyl bromide (10 g) in EtOH (75 ml) was added and the mixture refluxed for 1 hr. The soln was then cooled and filtered, the ppt washed with EtOH and recrystallised from EtOH, to yield white crystals (12.7 g) of the phenacyl ester. This ester (1g) was dissolved in 85% H_2SO_4 (14 ml) and left at room temp for 2 hr. The soln was then poured into ice-water to give the 4-phenyl-isocoumarin as white crystals (0.8 g), m.p. 123–4° (Found: C, 72.78%; H, 5.60%. $C_{17}H_{14}O_4$ requires: C, 72.33%; H, 5.00%.) $\tau_{(CDCl_3)}$ 2.57 d (1H, J = 2), 2.72 m (5H), 3.05 s (1H) 3.30 d (1H, J = 2), 6.12 s (3H), 6.60 s (3H). $\nu_{C=O}$ 1714 cm^{-1}. λ_{max}^{EtOH} 233, 285 and 350 nm.

5,7-Diacetoxy-4-phenylisocoumarin (**15**). 3,5-Dihydroxybenzoic acid (7.7 g) and phenacyl bromide (10 g) were dissolved in EtOH (120 ml). Triethylamine (7 ml) was added and the mixture left stirring at room temp for 24 hr. The mixture was then filtered, washed with $NaHCO_3$ aq, dried, and the solvent evaporated under reduced pressure to give a crystalline solid (5 g). This product (2 g) was dissolved in 85% H_2SO_4 (40 ml) at 0° and left at room temp for 24 hr. The soln was then poured onto ice and the ppt filtered off and recrystallised from EtOH water to give 5,7-dihydroxy-4-phenylisocoumarin (0.2 g). Acetylation with Ac_2O and pyridine gave **15** m.p. 166–7°. $\nu_{C=O}$ 1737 cm^{-1}. λ_{max}^{EtOH} 229, 270 and 330 nm. (Found; C, 67.00; H, 3.72%. $C_{19}H_{14}O_6$ requires: C, 67.45; H, 4.17.) $\tau_{(CDCl_3)}$1.93 d (1H, J = 2), 2.5–2.8 m (5H), 2.81 d (1H, J = 2), 2.98 s (1H), 7.72 s (3H), 8.70 s (3H).

6-Methoxyisoaurone (**16**). 2-Hydroxy-4-methoxyphenylglyoxylic acid (2g) was dissolved in EtOH (20 ml) and hydrazine hydrate (3g, 95%) added. This soln was then added to a soln of Na (3g) in EtOH (30 ml) and the mixture heated slowly under N_2 on an oil-bath until the bath temp reached 200° at which temp it was maintained for 15 min. The mixture was then cooled, dissolved in 50% HCl (60 ml), and extracted with ether. The ether layer was dried and evaporated under reduced pressure to yield a tan solid (1.3 g). This solid (1 g), benzaldehyde (0.55 g), Ac_2O (2 g), and triethylamine (0.5 g) were heated together for 1 hr at 90°. This mixture was poured into ice-water, and the ppt filtered off and subjected to

column chromatography on silicic acid using toluene-petroleum ether (1:1) to yield the isoaurone as yellow crystals (0.9 g) m.p. 115° (Lit.[25] 115°). (Found: C, 75.71; H, 5.34% $C_{16}H_{12}O_3$ requires: 76.18; H 4.79.)

Alternative preparation of 2-hydroxy-4-methoxyphenylacetic acid (17). 2-Benzyloxy-4-methoxyacetophenone (0.5 g) was added to thallium(III)nitrate (0.78 g) in MeOH (10 ml) containing perchloric acid (1 ml) and the soln stirred for 12 hr. The soln was filtered, the filtrate dissolved in 5 N NaOH (10 ml), and stirred for a further hr. The soln was then acidified with HCl and 2-benzyloxy-4-methoxyphenylacetic acid (0.4 g, 75%) filtered off. This acid (0.1 g) was dissolved in MeOH (20 ml), 10% Pd-C (0.1 g) added and the mixture hydrogenated for 12 hr. The soln was filtered and the solvent removed under reduced pressure to yield 2-hydroxy-4-methoxyphenylacetic acid (0.06 g) as a white solid.

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