

Photochemical Nitration by Tetranitromethane. Part XXXV.† A Possible Addition/Elimination Pathway in the Photochemical Reaction of 2,5-Di-*tert*- butyl-1,4-dimethoxybenzene and Tetranitromethane

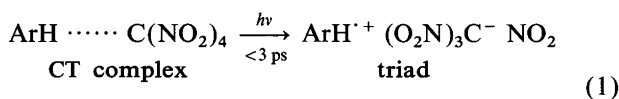
Jan Olof Svensson

Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden

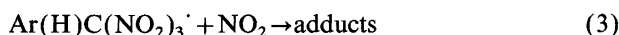
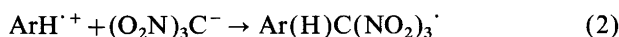
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The photolysis of the charge transfer complex of 2,5-di-*tert*-butyl-1,4-dimethoxybenzene (**1**) and tetranitromethane gives exclusively 4-*tert*-butyl-2,5-dimethoxynitrobenzene (**2**) in both dichloromethane and acetonitrile at room temperature. Photolysis in dichloromethane in the presence of trifluoroacetic acid (0.10–1.0 mol dm⁻³), gives 2,5-di-*tert*-butyl-1,4-benzoquinone (**3**) (6–25%), 5-*tert*-butyl-4-methoxy-1,2-benzoquinone (**4**) (9–25%) and 5-*tert*-butyl-4-methoxy-1,2-dihydroxybenzene (**5**) (13–25%) together with **2** (25–71%). Nitration of **1** with HNO₃/acetic anhydride or a solution of nitrogen dioxide in dichloromethane gives **2** as the main product, together with products **3–5**. It is suggested that **2** is formed in the photolysis by the decomposition of transient adducts, in which trinitromethyl and NO₂ have been added across the aromatic ring. The protonation of trinitromethanide by trifluoroacetic acid eliminates the nucleophile and thus inhibits the formation of adducts, and the products are then formed mainly by coupling of nitrogen dioxide with the radical cation **1**^{•+} or **1**.

The photochemical excitation of the charge transfer (CT) complex between an aromatic compound (ArH) and tetranitromethane (TNM) leads to a triad consisting of ArH^{•+}, nitrogen dioxide and trinitromethanide ion [eqn. (1)].¹

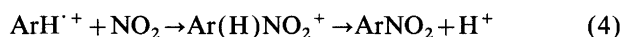


The first chemical step is the reaction between ArH^{•+} and trinitromethanide ion giving a neutral carbon radical [eqn. (2)] which subsequently reacts to give adducts with nitrogen dioxide [eqn. (3)].^{2,3}



Addition of trifluoroacetic acid (TFA) in an appropriate concentration to the reaction mixture prior to the photolysis, protonates the trinitromethanide ion and produces non-nucleophilic nitroform. The addition of acid will thus block the ArH^{•+}–trinitromethanide reac-

tion and allow slower reactions, such as coupling between ArH^{•+} and nitrogen dioxide, to dominate [eqn. (4)].



Preparative photolysis of naphthalene–TNM shows a dramatic change in the product distribution upon addition of TFA. With TFA present in a 1.5 mol dm⁻³ concentration, the yields of adducts and 1-nitronaphthalene were 2 and 37%, respectively, compared to 47 and 6.5% from the run without TFA, a change by a factor > 130.⁴ Since the adducts were found to be stable towards acid,⁵ the change must be due to elimination of trinitromethanide by protonation, whereby the coupling between ArH^{•+} and nitrogen dioxide is favoured. The yield of 2-nitronaphthalene with TFA added was ca. 0.7%, thus putting the ratio of 1-/2-isomer at > 50, similar to the ratio obtained in the coupling reaction between presynthesized naphthalene radical cation hexafluorophosphate and nitrogen dioxide.⁶

As part of a continuing study of the photolysis reactions of charge-transfer complexes of aromatic compounds, including methoxy-substituted naphthalene⁷ and benzene derivatives,^{8,9} with tetranitromethane (TNM), the reaction of 2,5-di-*tert*-butyl-1,4-dimethoxybenzene

† Part XXXIV, see Acta Chem. Scand. 50 (1996) 1121.

(1) with TNM has been investigated. This compound gives a very stable radical cation.^{10,11} The photochemistry of methoxy-substituted benzenes with tetranitromethane has also been investigated by Sankararaman *et al.*¹² In the following, arguments will be presented that most of the products isolated from the photolysis reactions arise from the rapid decomposition of transient adducts, the intermediacy of which is implicated by an altered product distribution upon changes in the reaction conditions.

Results

Photolysis of tetranitromethane and 2,5-di-tert-butyl-1,4-dimethoxybenzene (1) in dichloromethane and identification of products. Table 1 shows the product composition from the photolysis (filtered light, $\lambda > 435$ nm) of solutions of **1** (0.25 mol dm^{-3}) and TNM (0.50 mol dm^{-3}) in dichloromethane at three temperatures, 25, -20 and -50 °C. The solution after 1 h at -50 °C (conversion 40%) contained 98% of the nitro-*de-tert*-butylation product **2** and 2% of the 1,4-benzoquinone **3**, a decrease of the amount of **3** from 11% at 0.25 h (8% conversion). After 1 h at -20 °C (conversion 50%) the reaction mixture contained 88% **2** and 12% **3**, the amount of **3** decreasing to 4% after 6 h. After 1 h at 25 °C, the conversion was 81% and the solution contained only **2**; no other products were detected at lower conversions. Addition of TFA lowered the rate of conversion (Table 2), so that at $[\text{TFA}] = 1.0 \text{ mol dm}^{-3}$ the conversion after 6 h was only 25%. Upon irradiation of the photolysis mixture with $[\text{TFA}] = 1.0 \text{ mol dm}^{-3}$ the solution became dark green owing to a significant concentration of the radical cation of **1** ($1^{\cdot+}$). The colour change

Table 1. Yields of products from the photolysis of 2,5-di-tert-butyl-1,4-dimethoxybenzene (**1**, 0.25 mol dm^{-3}) and tetranitromethane (0.50 mol dm^{-3}) in dichloromethane.

$T/^\circ\text{C}$	t/h	Conversion(%)	Yield(%)	
			2	3
25	1	81	100	
-20	1	50	88	12
	2	62	95	5
	6	100	96	4
-50	0.25	8	89	11
	0.5	17	96	4
	1	40	98	2
	1.5	55	99	1
	2	100	99	1

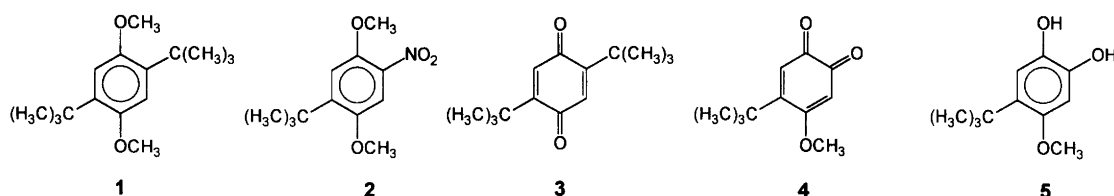


Table 2. Yields of products from the photolysis of 2,5-di-tert-butyl-1,4-dimethoxybenzene (**1**, 0.25 mol dm^{-3}) and tetranitromethane (0.50 mol dm^{-3}) with addition of trifluoroacetic acid (TFA) in dichloromethane.

$T/^\circ\text{C}$	$[\text{TFA}]/\text{mol dm}^{-3}$	t/h	Conversion(%)	Yield(%)			
				2	3	4	5
25	0.10	3.7	75	71	6	9	13
		0.25	23	42	16	21	21
		0.5	29	46	13	19	22
	1.0	1	54	49	11	19	21
		3	81	55	8	17	19
		6	25	25	25	25	25
-20	0.20	6	66	53	9	16	16

was not so pronounced at lower $[\text{TFA}]$. The product distribution was altered by the addition of TFA. The yield of **2** decreased while **3**, the 1,2-benzoquinone **4** and the dihydroxybenzene **5**, were formed. The change in product composition with respect to reaction time is shown in Table 2 for a reaction with $[\text{TFA}] = 0.20 \text{ mol dm}^{-3}$. Only minor changes were observed during the course of the reaction.

Photolysis in acetonitrile at 25 °C. Table 3 shows the product composition from the photolysis in acetonitrile. As in dichloromethane, **2** was the only product formed but the rate of conversion was lower than in dichloromethane, 85% at 3.5 h in acetonitrile compared to 81% at 1 h in dichloromethane. With 0.20 mol dm^{-3} TFA present the rate of conversion was lowered compared to the rate without TFA, from 62 to 48% at 2 h reaction time. The product distribution was altered by acid addition in a manner similar to the reaction in dichloromethane, products **3** (4%), **4** (6%) and **5** (6%) being formed at the expense of **2** (84%).

Table 3. Yields of products from the photolysis of 2,5-di-tert-butyl-1,4-dimethoxybenzene (**1**, 0.25 mol dm^{-3}) and tetranitromethane (0.50 mol dm^{-3}) in acetonitrile with the addition of trifluoroacetic acid (TFA) at 25 °C.

t/h	$[\text{TFA}]/\text{mol dm}^{-3}$	Conversion(%)	Yield(%)			
			2	3	4	5
2	0	62	100			
3.5		85	100			
6.5		100	100			
2	0.20	48	85	3	6	6
6.5		67	84	4	6	6

Nitration of 1 with nitrogen dioxide. Solutions of NO_2 in organic solvents actually contain predominantly N_2O_4 , since K_{diss} of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is in the range of 10^{-4} – 10^{-5} M. Since the rate constants pertaining to this equilibrium are high, NO_2 will always be available for participation in bimolecular processes with other species. The reaction between equivalent amounts of **1** and nitrogen dioxide in dichloromethane at 25°C (Table 4) gave mainly **2** (90%) together with **3** (2%) and **5** (8%), and at -50°C **2** (72%) together with **4** (20%) and **5** (8%). Upon addition of acid ($[\text{TFA}] = 0.1 \text{ mol dm}^{-3}$) the product distribution was altered in favour of **3** (10%), **4** (13%) and **5** (17%), but the main product was still **2** (60%).

Nitration of 1 with NO_2^+ . The nitration of **1** in HNO_3 -acetic anhydride yielded a mixture of **2**–**5** (Table 4).

Nitration of 2,5-di-tert-butyl-1,4-dimethoxybenzene radical cation (I^+) with nitrogen dioxide. The nitration of the radical cation (for preparation, see Experimental) with nitrogen dioxide yielded **2** (58%), **3** (5%), **4** (15%) and **5** (8%) (Table 4).

Discussion

The modes of formation of 2–5 in the photolysis of the 2,5-di-tert-butyl-1,4-dimethoxybenzene-tetranitromethane charge transfer complex. After formation of the triad [eqn. (1)], the radical cation ArH^+ has several competing product-forming pathways and, as recently shown,^{2,7,9,13} the fastest step is the reaction with the trinitromethanide ion [eqn. (2)]. When this step is blocked due to protonation of the nucleophile by trifluoroacetic acid, the coupling between ArH^+ and NO_2 becomes operative. Elimination of the faster pathway gives the radical cation a prolonged lifetime. As seen in EPR spectroscopic experiments, the addition of TFA ($[\text{TFA}] = 0.1 \text{ mol dm}^{-3}$) to a photolysed mixture containing **1** and TNM leads to an intensity increase of the EPR spectrum of the radical cation, by a factor 10 compared to irradiation without added TFA.²

Although no adducts in which the elements of TNM have been added across the aromatic ring have been observed in the photolysis, this pathway is assumed to

be the origin of **2** in the photolysis reaction. If compound **2** is formed by decomposition of adducts, the addition of acid would be expected to give rise to an altered product distribution, due to partial or complete elimination of the adduct pathway, and to a decrease in the rate of conversion, due to slower remaining pathways. The product forming reaction would then be expected to be either the coupling between the other two species formed in the initial triad, nitrogen dioxide and I^+ , or the nitration of **1** by NO_2 which has escaped the triad.

This is in essence what is being observed. The photolysis at 25°C in dichloromethane without TFA gave exclusively **2** (Table 1), while the NO_2 nitration of both compound **1** and the cation radical of **1** yielded other products as well (**3** and **5**, Table 4). Photolysis at lower temperatures (-20 and -50°C) gave only **2** and **3**, while the nitration of **1** with nitrogen dioxide at the same temperatures also gave **5** together with compound **4**. The NO_2^+ -mediated nitration also gave products **3**–**5** together with **2** (Table 4).

The addition of a nitrogen dioxide solution to **1** at -50°C (Table 4) resulted in a weak and transient change in colour due to the formation of I^+ , a colour change not seen when the reaction was performed at room temperature. A more pronounced transient colour appeared with TFA present at room temperature.

The nitro-dealkylation of **1** by nitrogen dioxide has been reported by Rathore *et al.*, although no products of oxidative dealkylation were identified.¹⁴ Oxidative dealkylation and nitro-dealkylation have earlier been reported in the NO_2^+ -mediated nitration of 2,5-disubstituted 1,4-dimethoxybenzenes.^{15–18}

Control experiments. In order to look for fragmentation and rearrangement reactions, presynthesized radical cation I^+ was kept under identical conditions as in the nitration reaction (Table 4) but without addition of NO_2 . After the reaction time (15 min) had elapsed, the solution contained only the unchanged radical cation, and no rearrangement products could be detected. Thus the products obtained in the nitration of the radical cation, do not arise from spontaneous decomposition of the radical cation. Further, compound **1** (with no TNM present) was treated with $[\text{TFA}] = 1.0 \text{ mol dm}^{-3}$ for 6 h, with and without irradiation. In both cases **1** was left

Table 4. Yields of products from nitration of 2,5-di-tert-butyl-1,4-dimethoxybenzene (**1**) and radical cation (I^+) by nitrogen dioxide in dichloromethane, and by HNO_3 in acetic anhydride (NO_2^+).

Substrate /mmol dm ⁻³	Nitrating agent /mmol dm ⁻³	T /°C	[TFA] /mol dm ⁻³	Yield(%)			
				2	3	4	5
1 (50)	NO_2 (50)	25	0	90	2	0	8
1 (50)	NO_2 (50)	25	0.1	60	10	13	17
1 (50)	NO_2 (50)	-50	0	72	0	20	8
I^+ (3.0)	NO_2 (9.0)	25	0	70	2	18	10
1 (83)	HNO_3 (92)	25	0	71	5	12	12

unaffected. This establishes that 3–5 are not formed by the action of TFA upon 1.

AM1 calculation and possible modes of adduct formation.

The calculated atomic charges on the ring carbon atoms of the radical cation of 1 are given in Fig. 1. Taking the calculation result and the steric hindrance into account it seems likely that trinitromethanide would attack the radical cation *ipso* to the methoxy group which would give a carbon radical 6 (Scheme 1), the stability of which would be increased by the presence of the *tert*-butyl group and the methoxy group. An attack by the nucleophile on C2 would be disfavoured both by the unfavourable charge on the carbon atom and by the large steric hindrance exercised by the *tert*-butyl group. Attack of nitrogen dioxide at C2 would subsequently give the sterically compressed diene 7, for which an easy elimination pathway would involve the loss of $(\text{CH}_3)_3\text{C}-\text{C}(\text{NO}_2)_3$ and give 2. The diene 7 is regarded as the precursor for compounds 4 and 5, via similar elimination reactions. The alternative coupling of nitrogen dioxide and 6 at C4 with C–N or C–O bond formation would give the diene 8, where X may be either NO_2 or ONO . The dienone 9 ($\text{X} = \text{NO}_2$ or ONO) would be formed after loss of $\text{CH}_3-\text{C}(\text{NO}_2)_3$. Upon loss of the

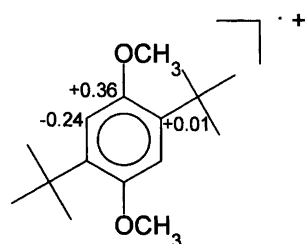
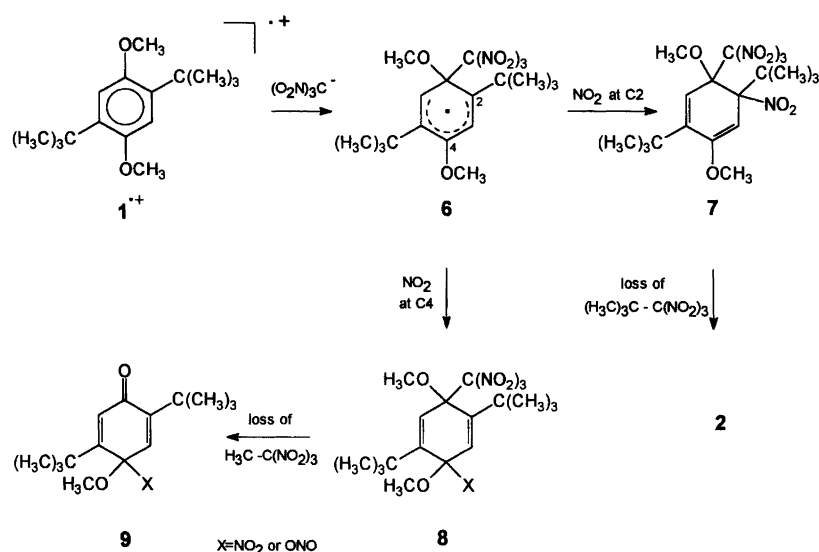
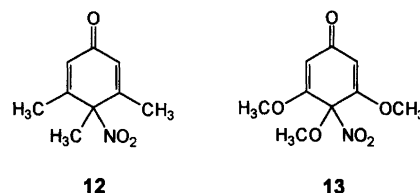
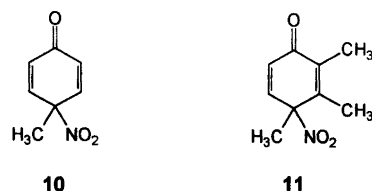


Fig. 1. Calculated (optimized AM1; UHF method) atomic charges on carbon atoms in the radical cation of 2,5-di-*tert*-butyl-1,4-dimethoxybenzene.

elements of CH_3-NO_2 or CH_3-ONO compound 3 would be formed from 9. The apparent decrease in the yield of 3 with higher conversion (Table 1) is regarded as a consequence of the formation of 3 in the initial part of the photolysis, the relative yield decreasing with higher conversion if only 2 is formed in the latter part of the photolysis. Compounds similar to 9 have been identified; 4-methyl-4-nitrocyclohexa-2,5-dienone (10) has been isolated in the photolysis reaction of tetranitromethane and 4-methylanisole.⁹ In the photochemistry of 1,2,3-trimethylbenzene and tetranitromethane both 2,3,4-trimethyl-4-nitrocyclohexa-2,5-dienone (11) and 3,4,5-trimethyl-4-nitrocyclohexa-2,5-dienone (12) have been isolated.¹⁹ 4-Nitro-3,4,5-trimethoxycyclohexa-2,5-dienone (13) has been isolated in the nitration of 1,2,3,5-tetramethoxybenzene with nitric acid-acetic anhydride.²⁰ This nitrodienone was converted slowly and quantitatively into the corresponding *p*-quinone in CDCl_3 in the presence of a trace of acetic acid, by the formal loss of CH_3NO_2 .



Scheme 1

The indications presented above for the formation of the main product **2** via the rapid decomposition of transient adducts (of the type **7**) rests mainly on the change in product distribution caused by acid addition and thereby inhibition of the formation of adducts. The lowered rate of conversion caused by the acid addition is a consequence of the elimination of the fast addition/elimination mechanism. In the photolysis without added acid the only products formed are **2** and **3**, which should be compared with the concomitant formation of **4** and **5** in the nitration of the parent compound **1** and **1**^{•+} with nitrogen dioxide or with HNO₃/acetic anhydride. Thus the difference in product distribution in the thermal nitration reactions compared to the photochemical nitration reactions supports the proposed addition/elimination mechanism. The fact that the proposed adduct **7** or **8**, with the trinitromethanide group *ipso* to the methoxy group, has not been isolated may be attributed to the presence of the methoxy group, which should facilitate the elimination of CH₃-C(NO₂)₃ or (H₃C)₃C-C(NO₂)₃, and thus make the adduct instable and difficult to detect or isolate. The same difficulty has been experienced to some extent in the case of 4-chloroanisole.⁸ In the photolysis of 1-methoxynaphthalene and TNM,⁷ evidence for the addition/elimination mechanism was found by the exclusive formation of the dehydrodimer when the photolysis was performed in the presence of added acid. Since photolysis in the absence of acid gave high yields of nitro compounds and no traces of the dehydrodimer, this indicated that the addition/elimination mechanism was responsible for the formation of the nitro compounds.

Experimental

Materials. A literature procedure was used for the synthesis of **1**.²¹ Tetranitromethane (Aldrich), nitrosonium tetrafluoroborate (Merck, *zur Synthese*) and acetonitrile (Merck, UVASOL) were used as received and dichloromethane (Merck, SupraSolv) was dried over 4 Å molecular sieves. Solutions of NO₂ in dichloromethane were made up as previously described.²²

Instruments. NMR spectra were recorded on a Varian XL 300 spectrometer, and assignments were confirmed by HETCOR and long range HETCOR. Mass spectra were recorded on a Jeol JMS SX-102 instrument. EPR spectra were recorded by the Upgrade version ESP 3220-200SH of a Bruker ER-200D spectrometer.

Photochemical reactions: general procedure. A solution of **1** (0.25 mol dm⁻³) and tetranitromethane (0.50 mol dm⁻³) in dichloromethane or acetonitrile (8 ml) was irradiated by a vertically placed 300 W tungsten lamp (Osram Ultravitalux), above which a combined IR filter and cooling plate (a flat cylindrical glass cell of 15 cm diameter and 5 cm thickness through which a constant flow of tap water was maintained) was located. On the

top of the glass plate the filter (cut-off at 435 nm) was placed. This arrangement maintained the temperature of the photolysed solution at 25(1) °C. The samples to be irradiated, kept in small, closed glass vials, were placed on the filter and irradiated for the appropriate reaction period, and small samples were withdrawn for analysis at appropriate intervals. For irradiation at low temperatures a doubly jacketed (vacuum/cooling liquid) vessel was employed, cooling being effected by means of a Colora cooling thermostat (-20 °C) or by ethanol-dry ice (-50 °C). The work-up procedure, involving evaporation of the solvent and excess tetranitromethane at oil pump vacuum, was conducted at a temperature of ≤0 °C. The crude product mixtures were stored at -78 °C and analysed (¹H NMR spectroscopy) as soon as possible.

The products were separated by chromatography on a silica gel column, using pentane/dichloromethane as eluents, and identified by NMR spectroscopy and mass spectrometry.

Warning

While we did not experience any incidents when working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits,²³ and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.

Radical cation of 1. The radical cation of **1** was synthesised by oxidation of **1** (0.12 mmol) with an equivalent amount of nitrosonium tetrafluoroborate in acetonitrile (10 ml) under vigorous argon bubbling.²⁴ After evaporation of the solvent the salt was washed with dry diethyl ether. The dark green cation radical salt (0.4 μmol) was dissolved in 0.70 ml TFA, and an EPR spectrum was recorded at room temperature. The EPR spectrum could be simulated by the following parameters: *a*^{OMe} = 0.311 (6H), *a*^{H3,6} = 0.0861 (2H), *a*^{tBu} = 0.0123 (18H) mT, in good agreement with those found in AlCl₃-CH₃NO₂.²⁵

4-tert-Butyl-2,5-dimethoxynitrobenzene (2). ¹H NMR (300 MHz, CDCl₃): δ 7.43 (s, H-6), 7.03 (s, H-3), 3.94 (s, 2-OCH₃), 3.85 (s, 5-OCH₃), 1.38 (s, *tert*-butyl). ¹³C NMR (300 MHz, CDCl₃): δ 151.8 (C-5), 147.3 (C-2), 146.6 (C-4), 136.7 (C-1), 113.5 (C-3), 108.4 (C-6), 57.1 (2-OCH₃), 55.7 (5-OCH₃), 36.6 (CMe₃), 29.0 (CH₃). MS (GLC inlet, EI, 70 eV): *m/z* 239 (80%), 224 (100), 209 (13).

2,5-Di-tert-butyl-1,4-benzoquinone (3). ¹H NMR (300 MHz, CDCl₃): δ 6.48 (s, H-3, H-6), 1.27 (s, *tert*-butyl), in agreement with literature data.²⁶ MS (GLC inlet, EI, 70 eV): *m/z* 220 (97%), 205 (100), 177 (62), 163 (63), 135 (27).

5-tert-Butyl-4-methoxy-1,2-benzoquinone (4). ¹H NMR (300 MHz, CDCl₃): δ 6.52 (s, H-6), 5.84 (s, H-3), 3.79

(s, OCH₃), 1.27 (s, *tert*-butyl). ¹³C NMR (300 MHz, CDCl₃): δ 187.5 (C-2), 183.1 (C-1), 157.5 (C-4), 156.9 (C-5), 129.8 (C-6), 109.7 (C-3), 56.0 (OCH₃), 35.4 (CMe₃), 29.6 (CH₃). MS (GLC inlet, EI, 70 eV): *m/z* 194 (63%), 179 (91), 123 (100).

5-*tert*-Butyl-4-methoxy-1,2-dihydroxybenzene (**5**). ¹H NMR (300 MHz, CDCl₃): δ 6.29 (s, H-6), 5.78 (H-3), 3.89 (OCH₃), 1.30 (s, *tert*-butyl). ¹³C NMR (300 MHz, CDCl₃): δ 181.6 (C-1), 178.8 (C-2), 170.7 (C-4), 159.0 (C-5), 125.8 (C-6), 103.4 (C-3), 56.4 (OCH₃), 36.4 (CMe₃), 29.7 (CH₃). MS (GLC inlet, EI, 70 eV): *m/z* 196.1105 (*M*⁺, 31%, calc. for C₁₁H₁₆O₃ 196.1099) 196 (33%), 181 (100), 166 (14).

Literature data²⁷ suggested the assignment of the spectral data of **5** to compound **4**. However, the assignments made here are based on high resolution mass spectroscopy with electron impact ionisation and earlier analysis was made by chemical ionization (ammonia/methane) at normal resolution.

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