

Electron-Transfer Reactions On Enol-Ethers Induced By Aminium Salts Syntheses of 1,2-Dioxetanes And/Or Ketones

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Abstract: Thermally stable 4-alkoxy-4-(aryl)spiro [1,2-dioxetane-3,2'-adamantanes] **2a-e** have been synthesized by reaction of oxygen-saturated methylene chloride solutions of alkoxy(aryl) methylened adamantanes **1a-e** with catalytic amounts of one electron oxidizing agents as tris-*p*-bromophenyl ammoniumyl and/or tris-*o,p*-dibromophenyl ammoniumyl hexachloroantimonates (reagents A,B). Similar reactions carried out on **1a-d**, under argon-atmosphere, yield adamantyl-arylketones **5a-c** together with the corresponding alcohols **6a-b**. Both processes most likely involve the formation of radical cation intermediates (**1⁺**), leading to the reaction products through chain electron-transfer mechanisms.

INTRODUCTION

The discovery that aminium salts, *hole catalysts*, can be easily prepared¹ and fruitfully employed to induce in a variety of electron-rich substrates single electron transfer processes has set the scene for a wide-ranging development of the chemistry of cation radical intermediates.²

Theoretical work and sophisticated analytical techniques, that support and permit the detection and characterization of these intriguing and elusive intermediates, have further given the opportunity to study their various modes of evolution,³ spurring their intense utilization in several synthetic applications.

Particularly valuable are: (a) the radical cation pericyclic reactions⁴ (b) the chain-induced radical cation oxygenation of strained olefins, dienes, cycloalkanes^{5,6} affording oxygenated derivatives such as 1,2-dioxetanes and 1,2-dioxolanes once thought to be characteristic of photosensitized Foote type and/or singlet oxygenation procedures.^{7,8}

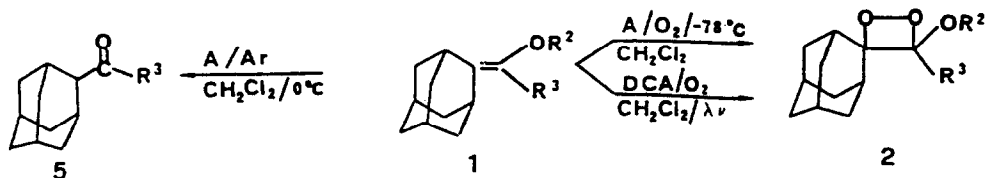
As a consequence other methodologies for the syntheses of 1,2-dioxetanes, previously confined to the area of interesting procedures, but of limited scope,⁹ have attracted the attention of several international groups.

In fact, these *hyperenergetic molecules*, in relation with their thermal stabilities, can be useful as controllable *dark sources* of electronically excited substrates,¹⁰ devising in the clinical laboratories new methodologies for bioassays, *i.e.* luminescent immunoassay (L.I.A.)¹¹

In recent communications,^{12,13} we have reported that 9,10-dicyanoanthracene (DCA)-photosensitization and/or catalytic amounts of tris *p*-bromophenylammoniumyl hexachloroantimonate [*p*-(BrC₆H₄)₃N⁺ SbCl₆⁻ A] [*E*^{red} = 1.17 V. vs SCE]¹⁻⁵ easily induce, in oxygen-saturated methylene chloride solutions, the conversion of alkoxy (aryl) methylened adamantanes **1** into the corresponding thermally stable 4-alkoxy-4-(aryl)spiro[1,2-dioxetane-3,2' adamantanes] **2**.

Both reactions most likely involve the intermediacy of donor radical cations **1⁺**, and consistent chemical evidence, coupled with cyclic voltammetric data, suggest a chain-radical cation oxygenation mechanism, which favourably competes with other modes of evolution. Similar reactions carried out under nitrogen and/or argon atmosphere yield adamantyl arylketones **5** together with the corresponding alcohol **14** (Scheme 1).

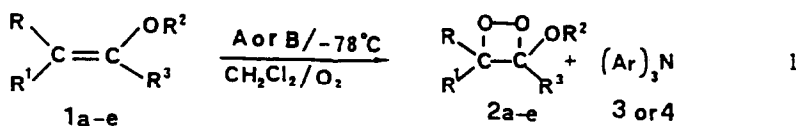
Scheme 1



We now report the full experimental results of a more systematic study carried out on other adamantyl enol ethers **1a-e**, easily converted into their corresponding 1,2-dioxetanes, or adamantyl-aryl ketones in relation to the reaction conditions. Other aminium salts, such as tris-(*o,p*-dibromophenyl) ammoniumyl hexachloroantimonate ($\text{Br}_2\text{C}_6\text{H}_4$) $_3\text{N}^+\text{SbCl}_6^-$ [$E^{\text{red}} = 1.66 \text{ V vs SCE}$] 1,5 **B**, a superior catalyst than **A**, have been fruitfully employed to carry out these reactions. 5

RESULTS AND DISCUSSION

By use of a general protocol, oxygen-saturated methylene chloride solutions of alkoxy (aryl) methylenediamantanes **1a-e** have been easily converted into their corresponding stable and isolable 1,2-dioxetanes **2a-e** together with traces of the corresponding amines **3** or **4** by reaction with catalytic amounts of reagents **A**, **B**, at low temperature (-78°C) (eq. 1).



1a. $\text{R}, \text{R}^1 = \text{Adamantyl}, \text{R}^2 = \text{CH}_3, \text{R}^3 = \text{C}_6\text{H}_5$; **1b.** $\text{R}^2 = \text{CH}_3, \text{R}^3 = 1\text{-C}_{10}\text{H}_7$; **1c.** $\text{R}^2 = \text{CH}_3, \text{R}^3 = 2\text{-C}_{10}\text{H}_7$; **1d.** $\text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5, \text{R}^3 = \text{C}_6\text{H}_5$; **1e.** $\text{R}^2 = \text{CH}_3, \text{R}^3 = \text{C}_{10}\text{H}_9$ (biphenyl)

Data concerning the experimental conditions of the oxidation of representative enol ethers, the chemiluminescent fragmentation results on the reaction products **2a-e**, together with their corresponding physical and spectral data are described in the Experimental Section.

The success of this easy synthetic procedure, residing to a great extent in the high stability and inertness of the spiroadamantane moiety, 15 might be rationalized on the basis of the peculiar features of the reagents involved.

In fact, cyclic voltammetric experiments on starting materials under inert and/or oxygen-saturated atmosphere (Fig. 1) clearly indicate that the one-electron oxidation of **1a-e** [E^{ox} ranging between 1.27-1.30 V. vs Ag/AgCl electrode] (Table 1), becomes irreversible in the presence of molecular oxygen.

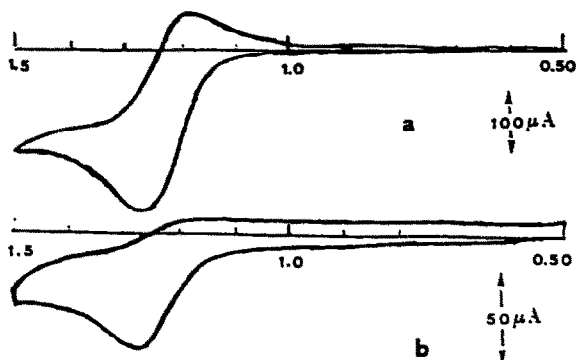


Fig. 1 Cyclic voltammograms on **1a** in oxygen-saturated (b), in argon-saturated solution (a)

On the basis of the chemical evidence available so far, this behaviour was unexpected. In fact, the cation radicals of unsaturated organic substrates, stabilized by heteroatoms or π -conjugation, have been reported to be inert towards molecular oxygen in spite of having fairly low oxidation potentials.¹⁶ On the contrary, it has been observed by Nelsen and co-workers on several Bredt's rule protected olefins such as biadamantylidene, which lead, in similar conditions, to a mixture of its remarkably stable corresponding 1,2-dioxetane, epoxide and spiroketone.⁵

The experimental observation that most of the oxidation current for the reversible **1a-e**/**1a-e**⁺ couple disappears when the solvent is saturated with molecular oxygen, is a straightforward evidence that radical cation intermediates react with molecular oxygen affording oxygenated radical cations (**1a-e O₂⁺**), which must be better oxidants than the starting materials.¹⁷ This will cause an electrochemical backward electrochemical process (ECbE) as reported by Feldberg and subsequently emphasized by Nelsen.^{5,17}

Both reagents A,B, notwithstanding their different oxidizing power, would induce an electron transfer reaction on substrates **1a-e** with the generation of the corresponding radical cations (**1a-e**⁺).

As reported in the Table 1, B is a stronger catalyst for the conversion of **1** to **2**, since the common first step is exothermic by over 9 kcal/mol.

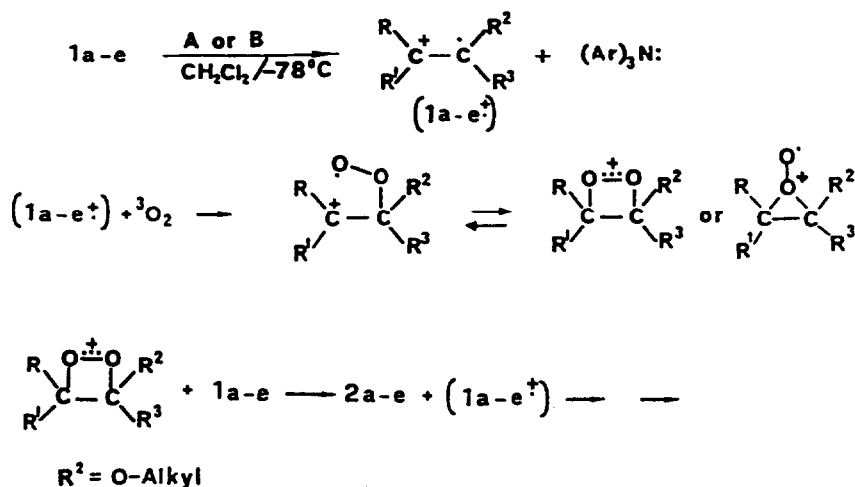
Table 1 Oxidation Potentials and the ΔG of Electron-Transfer from Enol-Ethers to A and B

Substrate	(E ^{ox}) ^a	ΔG (Kcal/mol) ^b	
1a	1.29	1.6 (A)	-9.6 (B)
1b	1.29		
1c	1.28	1.4	-9.9
1d	1.30	1.8	-9.4
1e	1.27	1.1	-10

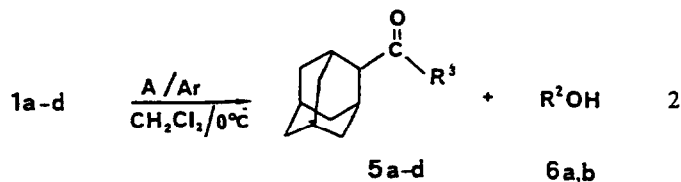
^aAll the oxidation potentials are reported in V vs Ag/AgCl in acetonitrile containing 0.1 tetraethylammonium perchlorate with a scan rate of 500 mV/sec. ^bA correction factor for Ag/AgCl to SCE was employed for the calculation of ΔG (see ref 18)

Indirectly, these data confirm that the driving force of the whole process is the following fast reaction of radical cation intermediates with molecular oxygen in the triplet state, as previously reported. This latter feature, as shown by low temperature electrochemical measurements,¹⁷ is of pivotal importance to demonstrate the exothermicity of the third step, as well as of the whole process (Scheme 2).

Scheme 2



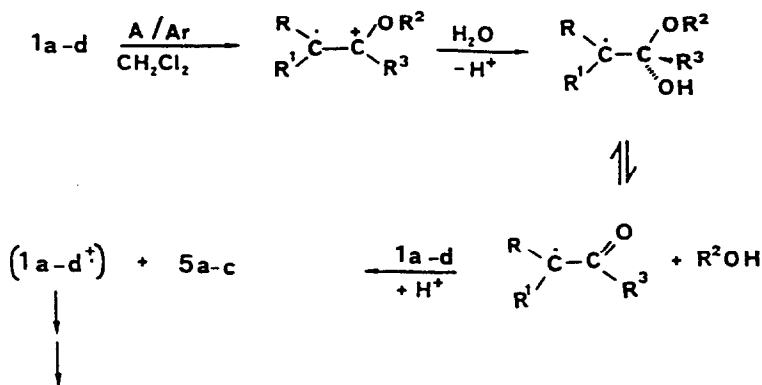
In reactions of ${}^3\text{O}_2$ with various radical cations, several oxenoid intermediates have been proposed, and their existence has been tentatively verified. In fact, compelling evidence concerning the intermediacy of an opened B-peroxycarbenium ion, have been reported by Bauld, and Nelsen, in the cycloaddition of olefin radical cations to unsaturated systems, and in the thermal induced-oxygenation of *syn* and/or *anti* 8-bicyclo [3,2,1]octylidene.^{4,5} Instead, the peroxide intermediate has been frequently suggested in certain photooxygenation reactions by several authors.⁷ However, notwithstanding the chemical proofs available so far, it seems, in accordance with Nelsen's results, that the simplest mechanism of enol-ethers oxidation induced by aminium salts would involve, as the only chain carrying oxidant, a three-electron π -bonded species, *namely* the dioxetane radical cation. As expected, 1,4-diazobicyclo [2.2.2] octane (DABCO)-controlled reactions do not afford the corresponding 1,2-dioxetanes, being the starting materials totally recovered. This is because DABCO's oxidation potential ($E^{\text{ox}} = 0.64 \text{ V. vs SCE}$)¹⁹ is lower than those of our starting materials, and so more easily oxidizable by aminium salts. On the other hand, the central role played by molecular oxygen has been clearly demonstrated carrying out, under argon atmosphere, similar reactions on enol ethers 1a-d with catalytic amounts of A.¹⁴ These latter slower reactions (3 h) afford, in high yield, the corresponding adamantyl-aryl ketones 5a-c, together with the corresponding alcohols 6a,b (eq. 2).



A better characterization of the alcohols, by-products of these processes, has been realized by performing the same reactions on *meta*, or *para*-dimethyl-*tert*-butylsilyloxy phenoxy (phenyl) methylened adamantanes 1g,f (see the experimental section).

A plausible mechanistic postulate would involve nucleophilic attack of adventitious water on radical cation intermediates (1a-d, g, f⁺), followed by proton loss with generation of hemiketal radical intermediates, in equilibrium with the alcohols and adamantyl-aryl ketone radicals. The subsequent electron-transfer with neutral materials and proton addition would afford the reaction products (Scheme 3).

Scheme 3



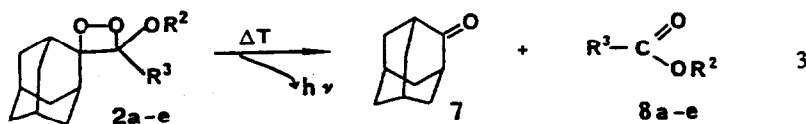
This mechanism is based on the statement that the standard oxidation potentials of ketones are larger than those of the corresponding enol ethers.²⁰

The faster reactions (less than 1h), and the incorporation of 18-oxygen, from labeled water, into adamantyl arylketones 5a-c * do not rule out a hydrolytic process (water as a source of H⁺).

Thus, the addition of a proton and the loss of an electron may have a similar or identical effect in the rearrangement of enol ethers.

However, several chemical evidence induce us to prefer the previous mechanistic pathway to the classical acid catalyzed conversion of enol-ethers into the corresponding ketones. In fact, similar results have also been observed carrying out the reactions on 1c,d in the presence of 0.02 mmol of 2,6-di-tertbutyl-4-methyl-pyridine as a base; DABCO, instead, totally inhibits the reactions, owing to its lower oxidation potential than those of the starting materials. DCA-sensitized photoreactions on 1a-d, carried out under argon atmosphere, lead to the same reaction products 5a-d with no traces of the corresponding dioxetane 2a-d, easily prepared in oxygen-saturated solutions. Furthermore, the rates of photo-processes are strictly related to the dryness of the reaction medium.¹³ DCA fluorescence-quenching by 1a-e, at diffusion controlled rate, via a s.e.t process, together with the e.s.r spectroscopic characterization of different enol ether radical cations by Symons²¹ substantiate the intermediate formation of the radical cations and their central role in this conversion.

Finally, the thermal chemiluminescent fragmentation process of the stable and isolable 1,2-dioxetanes 2a-e into 2-adamantanone 7 and the corresponding esters 8a-e, (eq.3), appear of relevant interest for the promising applications of these types of dioxetanes as labels in immunoassays.¹¹



CONCLUSIONS

These intriguing data point out the following facts (a) the reaction of molecular oxygen in the triplet state with thermally generated radical cations, *i.e.* not involving electronically excited states, can be fast enough to yield interesting oxygenation chemistry, leading to kinetically stable 1,2-dioxetanes, which are in some cases, useful target molecules for medical applications; (b) the evolution of enol-ether radical cations strictly depends on the reaction medium. Thus, further detailed investigations in the area are warranted.

EXPERIMENTAL SECTION

Melting points were taken on an electrothermal apparatus and are uncorrected. ¹H- and ¹³C-NMR spectra were recorded on a Varian XL-200 MHz instrument. IR, MS spectra were performed, respectively, on a Perkin-Elmer FT-1710 (KBr pellets), and on a Hewlett and Packard GC/Mass MSD 5970 instruments. GC analyses were carried out on a Hewlett and Packard gas chromatograph, model 5750 B, on columns (1/4" x 15 feet) packed with SP 2100 (5% on Supelcoport 100/120). TLC were performed on silica gel sheets with fluorescent indicator (Stratocrom SIF-Carlo Erba). Dichloromethane was purified by washing with sulphuric acid solution, distillation over calcium hydride and then stored in the dark under nitrogen atmosphere and over molecular sieves. The starting materials 1a-e have been synthesized through a modified Mc Murry's procedure²², devised by A. P. Schaap.²³ Aminium salts (A,B) have been synthesized following the procedure reported in literature.¹ DCA (Kodak Eastman Co) has been purified before the use.

Benzoyloxy (phenyl)methylidene adamantane 1d.

A black slurry of titanium coupling reagent was prepared, at -20°C, by slow addition of lithium aluminum hydride LiAlH₄ (3.8 g, 0.1 mol) to a stirred suspension of titanium trichloride TiCl₃ (30.8 g 0.2 mol) in dry tetrahydrofuran THF (250 ml) under nitrogen atmosphere. The mixture was warmed up to room temperature and triethylamine (C₂H₅)₃N (15ml) was added. To the refluxing mixture was gently added, over a 8h period, a THF solution (100 ml) containing equimolecular amounts of 2-adamantanone (1.5 g, 0.01 mol) and benzylbenzoate (2.12 g, 0.01 mol). After a further 12-h reflux period, the reaction mixture was cooled to room temperature and quenched by cautious addition of methanol (12 ml), and water (20 ml). The mixture was then diluted with a n-pentane/diethylether mixture (300 ml V:V 1:1) and passed rapidly through a florisil column. The organic solution was then concentrated by rotary evaporation, and the crude product was dissolved in methylene chloride (100 ml), washed four times with water (200 ml) and dried over anhydrous sodium sulphate. The solvent was removed in vacuo and the crude reaction product 1d (0.7 g, 21% yield) was purified by column silica gel chromatography (n-hexane/ethylacetate 10/1 as eluant), yielding 0.56 g of a white crystalline product m.p.= 49-50°C from n-heptane.

¹H-NMR (CDCl₃): δ=1.90-1.54 (m, 12 H), 2.62 (b, 1H), 3.18 (b, 1H), 4.42 (s, 2H),

7.38-7.24 (m, 10 H) ppm; ¹³C-NMR (CDCl₃): δ=28.24, 30.45, 32.30, 37.16, 38.76, 39.18, 71.26 ppm and consistent aromatic resonances; IR (KBr): ν=3028, 2950, 2901, 1486, 1445, 1597, 1265, 10888, 1062, 1023, 953, cm⁻¹; MS (m/e %) 330 (9), 211 (53), 105 (100), 91 (55), 77 (42)

C ₂₄ H ₂₆ O	calc.	C 87.22 %	H 7.93 %
(330.44)	found	87.13%	7.85 %

All the other starting materials, showing consistent physical and spectral data, have been prepared originally by A.P.Schaap and co-workers.²³

4-Methoxy-4-(phenyl)spiro[1,2-dioxetane-3,2'-adamantane] 2a: Typical procedure

To an oxygen-saturated solution of methoxy (phenyl) methylidene adamantane (1a; 0.0254 g, 0.1 mmol) in dry methylene chloride (5 ml) cooled at -78°C is rapidly added a methylene chloride (2 ml) solution of tris-p-bromophenyl ammoniumyl hexachloroantimonate (A; 0.016 g, 0.02 mmol) The blue colour of the solution fades and the reaction, monitored by T.L.C. (hexane:ethyl acetate 20:1 V:V as eluant) and/or by ¹H-N.M.R.spectroscopy (disappearance of the methoxy peak of vinyl ether) is judged complete within 15 min. The solvent is removed in vacuo and the residual solid is treated with cold n-hexane (10 ml) to eliminate, after filtration, the traces of the low soluble tris-p-bromophenylamines 3. Removal of n-hexane by rotoevaporation yields a white crystalline product 2a; 0.025 g (93%) m.p. 84-85°C;

¹H-NMR. (CDCl₃): δ = 0.90-1.92 (m, 12H), 2.16 (s, 1H), 3.05 (s, 1H), 3.22 (s, 3H), 7.38, 7.63 (m, 5H) ppm; ¹³C-NMR. (CDCl₃): δ = 25.97, 26.11, 31.60, 31.73, 32.27, 32.85, 33.33, 34.77, 36.48, 49.87, 95.40, 112.15, 128.18, 129.36, 134.73 ppm; I R. (KBr): ν = 3085, 2900, 1440, 1340, 1265, 1200, 1170, 1090, 945, 800, 745, 680 cm⁻¹

C ₁₈ H ₂₂ O ₃	calc	C 75.50%	H 7.74%
(286.37)	found	75.40%	7.52%

4-Methoxy-4-(1-naphthyl) spiro[1,2-dioxetane-3,2'-adamantane] 2b

Yield 95%; m.p. 119-120°C from hexane; ¹H-NMR. (CDCl₃): δ = 0.67-2.23 (m, 13H), 3.22 (s, 4H), 7.54-8.71 (m, 7H) ppm; ¹³C-NMR. (CDCl₃): δ = 25.86, 26.12, 31.56, 31.74, 32.24, 32.77, 33.47, 34.82, 36.59, 49.72, 96.32, 113.60, 124.95, 125.63, 125.69, 126.78, 129.10, 129.83, 130.83, 130.93, 133.98 ppm; I.R. (KBr): ν = 3030, 2910, 2838, 1600, 1520, 1455, 1255, 1205, 1105, 1066, 950, 777 cm⁻¹

C ₂₂ H ₂₄ O ₃	calc	C 78.54%	H 7.19%
(336.43)	found	78.21%	7.29%

4-Methoxy-4-(2-naphthyl) spiro[1,2-dioxetane-3,2'-adamantane] 2c

Yield 94%; m.p. 115-116°C from pentane; ¹H-NMR. (CDCl₃): δ = 0.90-2.00 (m, 12H), 2.22 (s, 1H), 3.11 (s, 1H), 3.24 (s, 3H), 7.50-8.30 (m, 7H) ppm; ¹³C-NMR. (CDCl₃): δ = 25.94, 26.08, 31.60, 31.72, 32.31, 33.08, 33.23, 34.88, 36.42, 50.00, 95.60, 112.33, 125.21, 126.47, 127.02, 127.63, 127.91, 128.67, 129.41, 132.13, 132.85, 133.61 ppm; IR. (KBr): ν = 3055, 3015, 2910, 2856, 1500, 1350, 1170, 1085, 1010, 950, 900, 815, 740 cm⁻¹

C ₂₂ H ₂₄ O ₃	calc.	C 78.54%	H 7.19%
(336.43)	found	78.38%	7.25%

4-Benzyloxy-4-(phenyl) spiro[1,2-dioxetane-3,2'-adamantane] 2d

Yield 94%; m.p. 105-106°C from petroleum ether 40-70 °C; ¹H-NMR. (CDCl₃): δ = 0.90-2.32 (m, 13H), 3.18 (s, 1H), 4.26 (d, 1H), 4.62 (d, 1H), 7.28-7.75 (m, 10H) ppm; ¹³C-NMR. (CDCl₃): δ = 25.91, 26.08, 31.65, 31.93, 32.30, 33.95, 34.84, 36.44, 64.18, 95.64, 112.02, 127.13, 127.36, 128.26, 128.29, 128.41, 129.47, 135.00, 138.05 ppm; IR. (KBr): ν = 3040, 3015, 2959, 2856, 1230, 1100, 1008, 972, 955, 802, 739 cm⁻¹

C ₂₄ H ₂₆ O ₃	calc.	C 79.53%	H 7.23%
(362.46)	found	79.22%	7.38%

4-Methoxy-4-(biphenyl) spiro[1,2-dioxetane-3,2'-adamantane] 2e

Yield 92%; m.p. 123 °C from petroleum ether 40-70 °C; ¹H-NMR. (CDCl₃): δ = 1.05-2.00 (m, 12H), 2.22 (s, 1H), 3.07 (s, 1H), 3.25 (s, 3H), 7.34-7.70 (m, 9H) ppm; ¹³C-NMR. (CDCl₃): δ = 25.91, 26.04, 31.54, 31.70, 32.32, 32.93, 33.17, 34.76, 36.40, 49.91, 95.45, 112.12, 126.80, 127.09, 127.69, 128.83, 129.14, 133.53, 140.19, 142.07 ppm; IR. (KBr): ν = 3040, 2905, 2850, 1600, 1440, 1390, 999, 935, 893, 828, 750, 728, 690 cm⁻¹

C ₂₄ H ₂₆ O ₃	calc.	C 79.53%	H 7.23%
(362.46)	found	79.16%	7.45%

A similar procedure has been followed by using the powerful one electron-transfer oxidizing agent: tris-*o*-p-dibromophenyl ammoniumyl hexachloroantimonate (B, 0.010 g, 0.01 mmol). In this case the green colour of solution fades within 5 min, obtaining traces of the amine 4 together with the same reaction products 2a-e.

The reactions carried out in the presence of DABCO (0.002 g, 0.02 mmol) are totally quenched.

Adamantyl-phenylketone 5a

To an argon-saturated solution of methoxy (phenyl) methylidene adamantane (1a; 0.0254 g 0.1 mmol) in methylene chloride (5ml), cooled to 0°C, is added a methylene chloride solution (2 ml) of tris p-bromophenyl ammoniumyl hexachloroantimonate (A; 0.016g 0.02 mmol). The blue colour of the solution fades slowly and the progress of the reaction can be monitored by GC until completion (3 h). The solvent is removed in vacuo and the residual solid is chromatographed over a silica gel column (petroleum ether 40/70: ethylacetate 9:1 v/v as eluant) yielding, nearly quantitatively, a white crystalline product 5a; m.p. 98°C, fully characterized by spectral data and elemental analysis.

¹H NMR. (CDCl₃) δ = 1.53-2.06 (m, 12H), 2.30 (s, 2H), 3.44 (s, 1H), 7.38-7.84 (m, 5H); ¹³C NMR. (CDCl₃) δ = 26.66, 27.09, 29.45, 31.90, 36.57, 37.99, 51.28, 127.17, 127.54, 131.25, 136.38, 203.22; IR. (KBr) ν = 3079, 3058, 2934, 2917, 1679, 1594, 1449, 1345, 1267, 1208, 1172, 1103, 1017, 950, 755, 692, 662, 638 cm⁻¹; MS (m/e %) 240 (52), 105 (100), 77 (53).

5a* MS (m/e) 242 (36), 240 (100), 107 (38), 105 (86), 77 (70)

C ₁₇ H ₂₀ O	calc.	C 84.95%	H 8.38%
(240.33)	found	84.73%	8.52%

The same product has been prepared by reaction on 1d, g, f. The corresponding alcohols, *namely*, benzylic alcohol 6b and *meta*, or *para*-dimethyl-tert-butylsilyloxy phenols 6c,d have been characterized by GC mass spectroscopy and comparison with authentic commercial, or synthesized samples. Acid-catalyzed conversions of *meta*, or *para*-dimethyl-tert-butylsilyloxy phenoxy (phenyl) methylidene adamantanes 1g,f lead to 5a and resorcinol, or hydroquinone respectively.

Adamantyl-2-Naphthylketone 5b

(yield 95%); mp 116; ¹H nmr (CDCl₃) δ = 1.55-2.11 (m, 12H), 2.37 (s, 1H), 3.59 (s, 1H), 7.52-8.32 (m, 7); ¹³C nmr (CDCl₃) δ = 27.57, 28.00, 30.47, 32.81, 37.47, 38.88, 52.29, 124.44, 126.59, 127.68, 127.96, 128.20, 129.02, 129.40, 132.57, 134.55, 135.13, 204.0; IR (KBr) ν = 3054; 3020, 1680, 1624, 1464, 1131, 967, 810, 746, cm⁻¹; ms (m/e) 290 (20), 155 (100), 127 (32).

5b* MS (m/e %) 292 (8), 290 (23), 157 (30), 155 (100), 77 (13)

C ₂₁ H ₂₂ O	calc.	C 86.85%	H 7.63%
(290.38)	found	86.71%	7.55%

Adamantyl-1-Naphthylketone 5c

(yield 95%); mp 155°C; ¹H NMR (CDCl₃) δ = 1.56-2.05 (m, 12H), 2.37 (s, 2H), 3.38 (s, 1H), 7.42-8.28 (m, 7H); ¹³C NMR (CDCl₃) δ = 27.70, 27.78, 29.91, 33.41, 37.28, 38.59, 55.29, 124.28, 125.20, 125.47, 126.24, 127.29, 128.41, 130.44, 130.96, 134.04, 137.08, 208.68;

IR (KBr) ν = 3083, 3045, 2914, 1671, 1507, 1454, 1168, 1095, 805, 773, 747 cm⁻¹; ms (m/e) 290 (15), 155 (100), 127 (28).

C ₂₁ H ₂₂ O	calc.	C 86.85%	H 7.63%
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(290.38) found 86.80% 7.54%

The characterization of the dioxetanes 2a-e has also been carried out by thermal chemiluminescent fragmentation followed by GC/mass spectroscopic characterization, and comparison with authentic samples of their cleavage products *i.e.* 2-adamantanone 7 and the corresponding esters 8a-e

7 MS: (m/e%) 150 (100), 117 (23), 93 (20), 91 (22), 80(82) 79 (97), 77 (23)

8a MS: (m/e %) 136 (35), 105 (100), 77 (65)

8b MS (m/e %) 186 (69), 155 (100), 127 (79), 77 (11)

8c MS (m/e %) 186 (63), 155 (100), 127 (86), 77 (14)

8d MS (m/e %) 212 (21), 167 (5), 105 (100), 77 (37)

8e MS (m/e %) 212 (70), 181 (100), 153 (30), 91 (77)

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