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ELECTRON-TRANSFER INDUCED CONVERSION OF ENOL-ETHERS INTO KETONES

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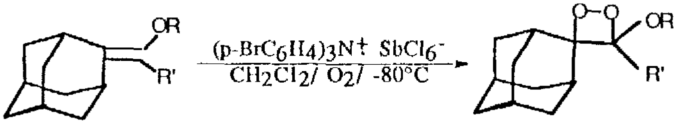
Abstract: Alkoxy (aryl)-methylidene adamantanes react with catalytic amounts of tris p-bromophenylammoniumyl hexachloroantimonate in CH_2Cl_2, under argon atmosphere, yielding adamantyl-arylketones together with the corresponding alcohols.The reaction most likely proceeds via an electron-transfer process

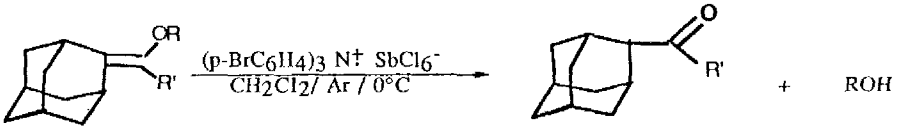
In a recent communication,[1] we have shown that the reactions of methoxy (aryl) methylidene adamantanes **1**, in oxygen saturated methylene chloride solution, with catalytic amounts of tris-p-bromophenylammoniumyl hexachloroantimonate ($(p\text{-}BrC_6H_4)_3N^{+\cdot}\ SbCl_6^-$, as an initiator, quantitatively led to the spiro dioxetanes **2** through a radical cation chain oxygenation mechanism (eq.1).



1

1 **2**

Proceeding in our research on the reactivity of, thermally generated, cation radicals,[2] we now report an easy and quantitative conversion of several enol ethers **1a-f**, in argon -saturated methylene chloride solution into the corresponding adamantyl-arylketones **3a-c** together with the alchools **4a-d** (eq. 2).



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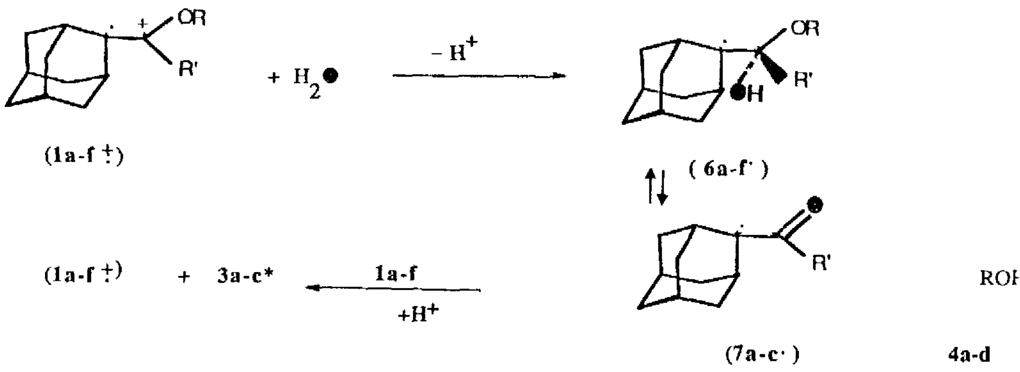
1a-f **3a-c** **4a-d**

1a R= CH_3; R'= C_6H_5. **1b** R= CH_3; R'= 1-$C_{10}H_7$. **1c** R=CH_3; R'= 2-$C_{10}H_7$. **1d** R=$C_6H_5CH_2$; R'=C_6H_5
1e R=C_6H_5; R'=C_6H_5. **1f** R=C_6H_4 p-$OSi(CH_3)_2C(CH_3)_3$; R'=C_6H_5

Typical experimental conditions for the synthesis of adamantyl-aryl ketones **3a-c** are as it follows: **1a-f** (0.1 mmol) are dissolved, at 0°C, in dry and freshly distilled methylene chloride (5 ml) under argon atmosphere, and a freshly prepared methylene chloride solution of the aminium salt (0.01-0.03 mmol in 5 ml) [3] added. The progress of the reactions can be monitored by gc until completion (3, 4h), and the reaction mixtures filtered on a short silica gel column to remove trace of the aminium salt; The solvent is removed in vacuo and the reaction products,isolated by column chromatography (silica gel, petroleum ether: ethylacetate 9:1) as white crystalline products, have been identified by physical (mp) and spectral data (ir, ^1H,^{13}C nmr's)[6]. Further characterization, above all, for the alcohols **4b-d** has been performed by gc/mass spectroscopy[7]

The only aspect that could be questioned in this classical conversion of enol-ethers into the corresponding ketones is the actual operating mechanism. In fact, this conversion can be successfully performed in hydrolytic acid or base conditions as extensively reported[8,9]. Anyway, the powerful aminium salt oxidant (E^{red}= 1.15 V *vs* Ag/Ag$^+$ electrode)[8] can induce an easy one-electron transfer reaction on our substrates (oxidation potentials in the range 1.27-1.30 V *vs* Ag/Ag$^+$ electrode in $CH_3CN/Bu_4N^+ ClO_4^-$) [1] with the formation of the corresponding cation radicals and neutral amine **5**. In oxygen atmosphere, these cation radicals react with oxygen affording the corresponding dioxetanes **2a-f**. Thus, a plausible mechanistic postulate for the conversion of the cation radical intermediates into ketones **3a-c** would involve a nucleophilic attack of adventitious water on the cation radicals, followed by proton loss with the generation of hemiketal radical intermediates **6**˙ in equilibrium with the alcohols **4a-d** and adamantyl-aryl ketone radicals **7**˙. The subsequent electron transfer with the neutral substrates **1a-f** and proton addition would convert **7**˙ into **3a-c***. This mechanism, substantiated by the perceptive studies of Gilbert *et al.*[10] and by the e.s.r. spectroscopic characterization of cation radicals of enol ethers and of their hydrated radicals by Symons *et al.*,[11] has also been tested, carrying out similar reactions on **1c-e** in the presence of trace amounts of 18-oxygen labeled water (33%) and analyzing the reaction products by gc/mass spectroscopy. The faster reactions, (less than 1h), the incorporation of 18-oxygen only into the ketones **3a-c***[12] make plausible, although it does not rule out the hydrolytic process (water could be the source of H^+), the mechanism described below .



Anyway, the chemical proofs that induce us to prefer this mechanistic pathway to the classical acid catalyzed conversion of enol ethers into the corresponding ketones are the following: (a) Similar results have been also observed carrying out the reactions on **1c,d** in the presence of 0.02 mmol of 2,6-di-tert-butyl-4-methyl-pyridine as a base; (b) the selective conversion of **1f** into **3a** together with p-dimethyl-tertbutyl silyloxy-phenol; (c) the 9,10-dicyanoanthracene (DCA)- sensitized photooxygenation of our substrates, in methylene chloride solution, afford the corresponding 1,2-dioxetanes through a chain electron transfer mechanism, as described in the previous communication13, instead, the same reactions, carried out under argon atmosphere, lead to the corresponding ketones with no traces of the dioxetanes, and the rate of the conversion is strictly related to the dryness of the reaction medium[14]; (d) the 2,3,5,6-tetrachloro-p-benzoquinone (TCB)-sensitized photooxygenations of our substrates in methylene chloride solution afford the corresponding spiro 1,2-dioxetanes **2a-f** together with variable amounts 5-30% of the ketones **3a-d**. in relation to the purity (water content) of the solvent. These last photochemical results substantiate our hypothesis. In fact, dioxetanes and ketones in the (TCB)-sensitized photooxygenations of our substrates can be rationalized on the basis of the peculiar physical properties of the sensitizer, excitable in the triplet state (E_T = 68 Kcal/mol)[15] and so able to generate, by energy-transfer to molecular oxygen, singlet oxygen, which on reaction with our substrates would afford dioxetanes **2a-f**.[16] Since, (TCB) has an exceedingly low reduction potential (E^{red} = 0.02 V vs SCE)[17] and so it is able to induce, better than (DCA)[18], electron transfer processes on our substrates with the generation of cation radicals (1a-f$^{\bullet +}$), which conversion into ketones could also be described as reported by us and by Gassman and co-workers in the photosensitized desilylation of silyl enol-ethers[19]

Further work in the area is warranted, not only on more simple enol-ethers, but also on other classes of organic substrates such as epoxides.

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2) Ciminale, F.; Lopez, L.; *Tetrahedron Lett.* **1985**, 789; Lopez, L.; Calò, V.; Stasi, F. *Synthesis* **1987**, 947.
3) The powerful ammoniumyl salt oxidant gives chemically reversible CV in methylene chloride (0.1 *M in* n-$Bu_4N^+ClO_4^-$ at a platinum electrode, E^{red}= 1.17 V vs SCE).(see ref. 4) The substrates **1a-e** give chemically reversible CV curves (E^{ox} =1.27-1.30 V vs Ag/Ag^+ in CH_3CN/ $Bu_4N^+ClO_4^-$). On the basis of these values it is likely that a set process, leading to the cation radicals (**1a-e**$^{+}$), might be operative, being this step endoergonic for less than 3 Kcal/mol (see ref. 5).
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6) **3a** (yield 92%); mp=98°C; ^1H nmr ($CDCl_3$) d 1.53-2.06 (m ,12H), 2.30 (s, 2H), 3.44 (s, 1H), 7.38-7.84 (m, 5H); ^{13}C nmr ($CDCl_3$) d 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) n 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).

   3b (yield 95%); mp 155°C; ^1H nmr ($CDCl_3$) d 1.56-2.05 (m, 12H), 2.37 (s, 2H), 3.38 (s, 1H), 7.42-8.28 (m, 7H); ^{13}C nmr ($CDCl_3$) d 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) n 3083, 3045, 2914, 1671, 1507, 1454, 1168, 1095, 805, 773, 747 cm^{-1}; ms (m/e) 290 (15), 155 (100), 127 (28).

3c (yield 95%); mp 116; ^{1}H nmr ($CDCl_3$) d 1.55-2.11(m, 12H), 2.37 (s, 1H), 3.59 (s, 1H), 7.52-8.32 (m, 7); ^{13}C nmr ($CDCl_3$) d 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) n 3054; 3020, 1680, 1624, 1464, 1131, 967, 810, 746, cm^{-1}; ms (m/e) 290 (20), 155 (100), 127 (32).

7) The benzylic alchool **4b** and the phenols **4c,d** have been characterized by gc/mass spectroscopy and /or comparison with authentic commercial samples.

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12) 3a*18-oxygen labeled ms (m/e) 242 (36), 240 (100), 107 (38), 105 (86), 77 (70).
3c*18-oxygen labeled ms (m/e) 292 (8), 290 (23), 157 (30), 155 (100), 77 (13).

13) Lopez, L.; Troisi, L.; Rashid, S.M.K.; Schaap, A.P. previous communication.

14) The methylene chloride has been purified as usual, distilled twice on $P_2 0_5$ and stored on molecular sieves.

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