The first example of noncatalytic *C*-alkylation of arylamines by *p*-methylenequinones

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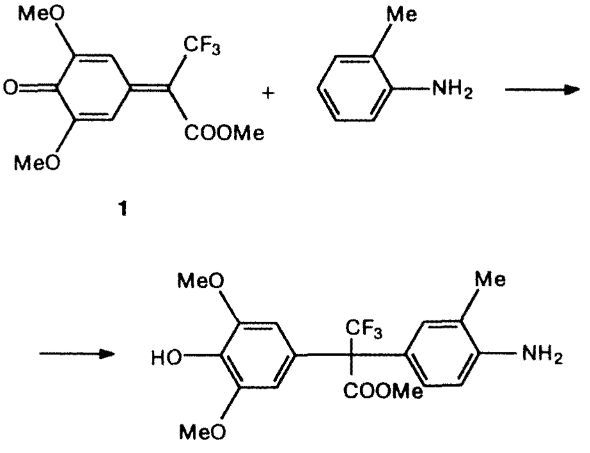
In the absence of a catalyst, *p*-methylenequinones react with arylamines to form either charge-transfer complexes or products of 1,6-addition[1,2] to the N atom. We have found that methylenequinones are capable of entering noncatalytic *C*-alkylation reactions of aromatic compounds. Thus, 2,6-dimethoxy-α-methoxycarbonyl-α-trifluoromethyl-*p*-methylenequinone[3] (**1**) with *o*-toluidine in benzene at 20 °C forms methyl α-(4-aminophenyl-3-methyl)-α-(3,5-dimethoxy-4-hydroxyphenyl)-β,β,β-trifluoropropionate (**2**) in 6 days.



2

The yield of compound **2** was 80.6%, m.p. 157—159 °C, R_f (acetone—CCl_4, 1 : 3) 0.45. ^1H NMR (acetone-d_6), δ: 2.05 (s, 3 H, Me); 3.35 (s, 2 H, NH_2); 3.65 (s, 6 H, 2 OMe); 3.75 (s, 3 H, COOMe); 6.40 (s, 2 H, H(2), H(6)); 6.60 (d, 1 H, H(5), $J_{H,H(6')}$ = 8.8 Hz); 6.74 (dd, 1 H, H(6'), $J_{H,H(5')}$ = 8.8 Hz, $J_{H,H(2')}$ = 1.5 Hz); 6.77 (br.s, 1 H, H(2')); 8.74 (s, 1 H, OH). ^{19}F NMR (DMSO-d_6), δ: 16.1 (s, 3 F, CF_3). Found (%): C, 57.14; H, 5.01; N, 3.51; F, 14.29. $C_{18}H_{20}F_3NO_5$. Calculated (%): C, 55.81; H, 5.17; N, 3.61; F, 14.73.

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Chemiluminescence of $Ru(bpy)_3Cl_2$ complex during the thermolysis of diphenyldiazomethane in the presence of oxygen

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Chemiluminescence (CL) during the thermolysis of diphenyldiazomethane, Ph_2CN_2, in the presence of oxygen has been observed previously.[1] It has been shown that the reaction of the initial Ph_2CN_2 with carbonyl oxide $Ph_2C^{\cdot}—O—O^{\cdot}$, which forms in the reaction of carbene Ph_2C: with oxygen, results in the

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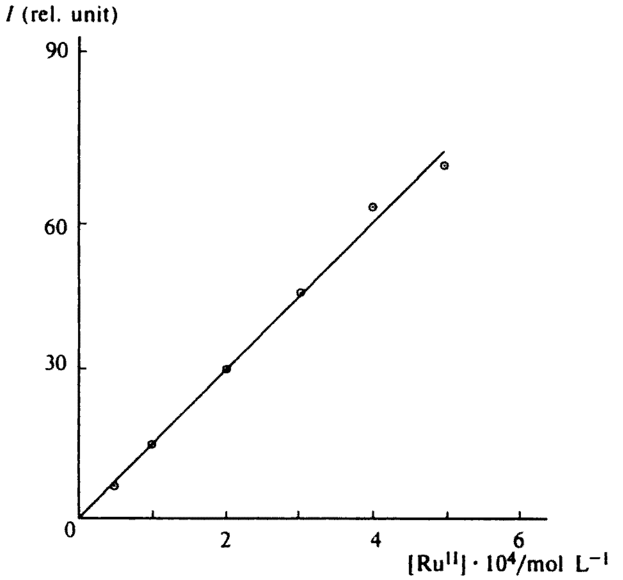

Fig. 1. Dependence of the intensity of CL on the concentration of Ru^{II} ($[Ph_2CN_2] = 10^{-3}$ mol L^{-1}).

formation of benzophenone in the triplet excited state (^3BP).

We have established that the CL observed in this reaction is activated efficiently by the Ru^{II} complex. In the presence of $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridyl, $[Ru^{II}] = (0.5—5.0) \cdot 10^{-4}$ mol L^{-1}), the intensity of CL increases 10—100 times during the thermolysis of Ph_2CN_2 in acetonitrile (55—75 °C, $[Ph_2CN_2] = 10^{-3}$—10^{-2} mol L^{-1}) with continuous bubbling of an argon—oxygen mixture with different contents of O_2 ($[O_2] = (10^{-3}$—$3.5) \cdot 10^{-3}$ mol L^{-1}). In the CL spectrum, the absorption band of ^3BP disappears completely and the luminescence band of Ru^{II} appears, which coincides with the spectrum of its photoluminescence (the spectra were recorded on an MZD-2M monochromator, $\Delta\lambda$ = 5 nm). In the range of 580—650 nm, the intensity of CL increases proportionally to the increase in the concentration of Ru^{II} (Fig. 1)

This indicates that Ru^{II} is not a simple acceptor of excitation energy from ^3BP, but participates directly in the chemiexcitation stage.[2] At the same time, in the whole temperature and concentration range studied the decay of CL occurs according to the first-order law and is independent of the content of the activator. Since no luminescence is observed during the bubbling of Ar through the reaction solution, we conclude that highly reactive oxygen-containing intermediate compounds are involved in the chemiexcitation of Ru^{II}. It is likely that one such compound is diphenylcarbonyl oxide $Ph_2C^{\cdot}—O—O^{\cdot}$, which also participates in the oxidation of the bipyridyl ligand. The oxidation of the ligand in the complex with Ru^{II} results in a change in the absorption and luminescence spectra and corresponds to the formation of hydroxy derivatives of the bipyridyl ligand in the complex.[3] In our opinion, Ru^{II} is excited during the reaction with $Ph_2C^{\cdot}—O—O^{\cdot}$ according to the mechanism of reversible electron transfer, which is known to be a mechanism of chemically induced electron-exchange luminescence:[4]

$$\begin{aligned}
&Ph_2C^{\cdot}{-}O{-}O^{\cdot} + Ru^{2+}(bpy)_3 \rightarrow \\
&\quad\rightarrow \{[Ph_2C^{\cdot}{-}O{-}O^{-} + Ru^{3+}(bpy)_3] \rightarrow \\
&\quad\rightarrow [Ph_2C{=}O^{-\cdot} + Ru^{3+}(bpy)_2bpy{-}OH]\} \rightarrow \\
&\quad\rightarrow [Ph_2C{=}O + Ru^{*2+}(bpy)_2bpy{-}OH] \rightarrow \\
&\quad\rightarrow Ph_2C{=}O + Ru^{2+}(bpy)_2bpy{-}OH + h\nu,
\end{aligned}$$

where $Ru^{2+}(bpy)_2bpy—OH$ is the hydroxy derivative of the Ru^{II} complex.

In this case, the excitation yield of Ru^{II} (φ_{Ru^*}) is equal to 0.15, which is close to the value of φ_{Ru^*} for the reaction with 1,2-dioxetane.[5]

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