First Evidence of a Single Electron Transfer Process from a Two-heteroatom-centred Anion. Easy Generation of Amidyl Radicals

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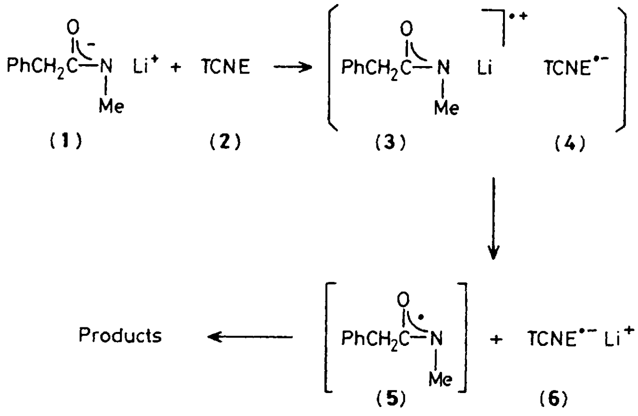
The two-heteroatom-centred amidate anion reacts with tetracyanoethylene (TCNE) in a single electron transfer process to afford TCNE$^{\bullet-}$ and amidyl radicals.

In the last 20 years numerous investigations have shown that single electron transfer (SET) processes are involved in a wide variety of organic reactions.[1] Anions, such as enolates,[2] thiolates,[3] Grignard reagents,[4] or aminyl anions,[5] are able to transfer an electron to substrates with sufficiently positive reduction potentials. However, to our knowledge, no SET process from a two-heteroatom-centred anion, such as the amidyl anion, has been described so far. We now report the first evidence of a SET process from an amidyl anion to tetracyanoethylene, TCNE, and our preliminary study on the reactivity of the resulting amidyl radical.

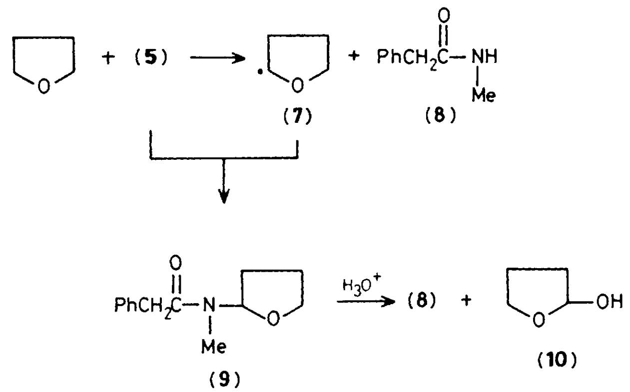
The addition of a stoicheiometric amount of tetracyanoethylene (**2**) to a 0.25 M solution of *N*-lithio-*N*-methylphenylacetamide (**1**) in anhydrous tetrahydrofuran, gives rise to the immediate appearance of a deep red colour. This new solution was found to decolorize diphenylpicrylhydrazyl (DPPH) and shows an intense and steady e.s.r. signal. The e.s.r. spectrum is that characteristic of TCNE$^{\bullet-}$ without any superimposed set of peaks.

The above observations can be rationalized in terms of a SET process from the anion (**1**) to TCNE (**2**) with initial formation of a radical ion pair (**3**,**4**) which is highly unstable owing to the presence of the lithioamidyl radical cation (**3**).[6] This radical ion pair generates the amidyl radical by loss of the lithium cation to afford finally the observed reaction products, whose nature depends on the reaction conditions, especially on the type of solvent used (see Scheme 1). In THF solution the amidyl radical (**5**) reacts with the solvent to afford, after acidic aqueous work-up, the starting amide (**8**) and 2-hydroxytetrahydrofuran (**10**) as the main products, as well as a small amount of γ-butyrolactone (see Scheme 2).

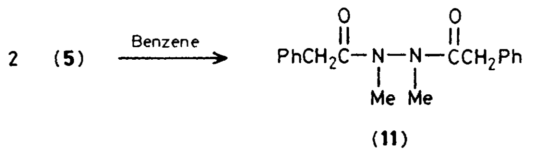
The formation of compounds (**8**) and (**10**) can be explained by assuming that the amidyl radical (**5**) abstracts the α-hydrogen from THF to yield the starting amide (**8**) and the 2-tetrahydrofuryl radical (**7**), which then couples with the amidyl radicals (**5**) that are further generated in the solution to afford the amidoacetal (**9**). This is hydrolysed in the workup yielding compounds (**8**) and (**10**).[7] The γ-butyolactone formed as a side product could well arise from the amidoacetal (**9**) acting as a hydrogen donor towards amidyl radicals or by partial oxidation of 2-hydroxytetrahydrofuran (**10**) in the course of the work-up for the elimination of the TCNE$^{\bullet-}$ Li$^+$. The role of amidyl radicals (**5**) as intermediaries can be ascertained by performing the reaction of TCNE and *N*-lithio-*N*-methylphenylacetamide in anhydrous benzene. Under



Scheme 1



Scheme 2



Scheme 3

these conditions, as no hydrogen donor is present, the amidyl radicals (**5**) undergo dimerization[8] to afford *N,N'*-dimethyl-*N,N'*-di(phenylacetyl)hydrazine (**11**),† in *ca.* 60% isolated yield (Scheme 3).

Photochemical methods have been used previously for the generation[9] and e.s.r. characterization[10] of amidyl radicals but suffer from the drawback of the simultaneous formation of a reactive radical partner in the homolytic cleavage of a N–Z bond[9] that could interfere in the study of the chemistry of these species and limits their synthetic use. The possibility now found by us, of using SET processes involving *N*-lithioamides and TCNE to generate amidyl radicals accompanied by an inert radical partner offers new potential in the study of the chemistry of these transient reactive species.

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† Selected data for the characterization of compound (**11**): m.p. (recrystallized from water) 138—140 °C; ^{1}H n.m.r. ($SiMe_4$, $DCCl_3$) δ 7.1 (s, 5H), 3.5 (s, 2H), 2.7 (d, 3H); ^{13}C n.m.r. ($SiMe_4$, $DCCl_3$) δ 172.46 (s), 134.56 (s), 129.45 (d), 129.08 (d), 127.51 (d), 43.60 (t), 26.58 (q); i.r. (Nujol) ν 1630 and 1600 (C=O) cm^{-1}, no absorption is detected in the 3100—3500 cm^{-1} region.

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