Formation of Fluoren-9-ylidenesuccinonitrile by Addition of Electrogenerated $^-CH_2CN$ Anions to Fluoren-9-one and Fluoren-9-ylideneacetonitrile

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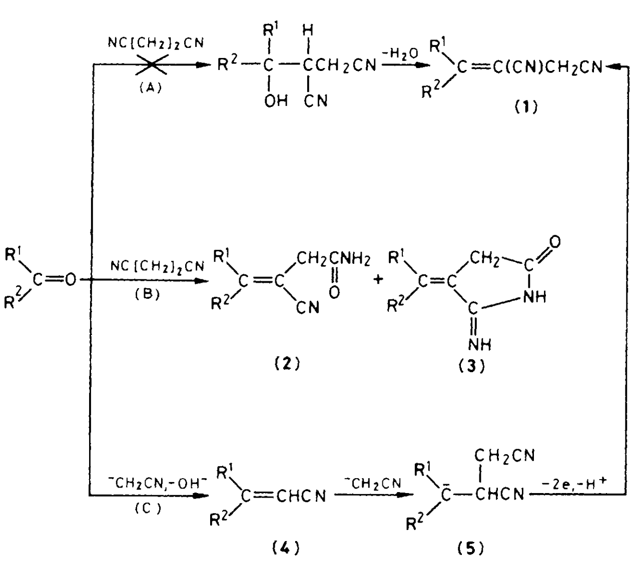
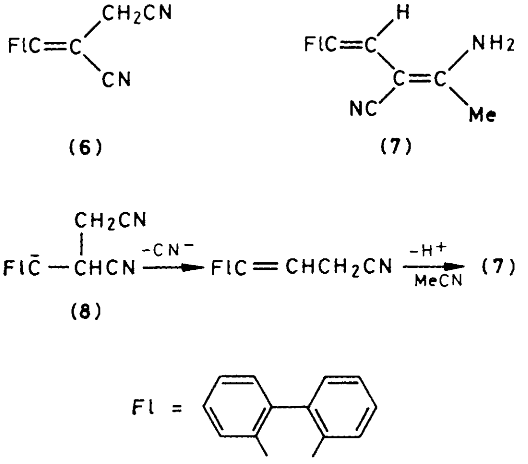
When $^-CH_2CN$ anions are electrogenerated in acetonitrile addition occurs to fluoren-9-one (FlC=O) or fluoren-9-ylideneacetonitrile (FlC=CHCN) to give the dinitrile derivative FlC=C(CN)CH_2CN as the major product, whereas attempts to synthesize it by condensation of fluorenone and succinonitrile have failed.

The chemical synthesis of dinitrile derivatives of type (**1**) would not be expected from an aldol-type condensation of succinonitrile with an aldehyde or a ketone (path A of Scheme 1). The analogy between the Stobbe condensation[1] and the condensation of succinonitrile with aliphatic or aromatic aldehydes and ketones has been established.[1–4] Compounds of types (**2**) and (**3**) are obtained with Bu^tOK in Bu^tOH,[4] path (B). Path (C) suggests a method for the preparation of the dinitriles (**1**) in acetonitrile from an aldehyde or a ketone. The addition of $^-CH_2CN$ anions to the carbonyl compound would lead to the intermediate activated olefin (**4**) which would be further attacked by $^-CH_2CN$. The formation of (**1**) according to path (C) requires that the following two conditions be fulfilled. (a) Attack by $^-CH_2CN$ should occur on the carbon atom α to the nitrile group of (**4**). This site of attack would be favoured if the anion (**5**) is stabilized by delocalisation. In the case of the alkenes PhRC=CHCN (R = H, Me, or Ph), the attack by electrogenerated $^-CH_2CN$ proceeds exclusively at the β-carbon atom.[5–9] (b) An oxidising species should be present which allows the oxidation of the intermediate anion (**5**) to (**1**).

We have observed that both conditions are met when $^-CH_2CN$ anions are electrogenerated; addition occurs to fluoren-9-one or to fluoren-9-ylideneacetonitrile. The dinitrile (**6**) has been prepared in yields (isolated) of up to 43% by the electrochemical route. In a typical procedure, azobenzene (2 mM) was reduced to its dianion at -2 V *vs.* S.C.E. (saturated calomel electrode) in MeCN–dimethylformamide (DMF) (1 : 10) with a mercury pool cathode and 0.1 M Bu_4NPF_6 as supporting electrolyte, under an atmosphere of argon. This procedure generates $^-CH_2CN$ anions from the MeCN.[5,6,10] Fluoren-9-one (1 mM) was then added and the mixture left for 2—3 h. Two main products were identified after column chromatography: (**6**) (43%) and (**7**)[11] (23%).



Scheme 1



Scheme 2

We have discussed elsewhere[11] the origin of (**7**) when electrogenerated $^-CH_2CN$ anions add to fluorenone. Attack by $^-CH_2CN$ on the carbon atom β to the nitrile group of fluoren-9-ylideneacetonitrile has been suggested.[11] According to path (C) in Scheme 1, (**7**) can also result from cyanide elimination (Scheme 2).

Traces of oxygen cause the oxidation of (**8**) to (**6**). The oxidation potential of the intermediate anion (**8**) is not known but should be in the same range as that of $\mathrm{Fl\bar{C}H^-}$ (E_0 = −0.67 V *vs.* S.C.E. in DMF[12]) or $\mathrm{Fl\bar{C}Me}$ (E_0 = −0.78 V *vs.* S.C.E. in DMF[13]). It is therefore sufficiently negative to allow (**8**) to reduce traces of oxygen whose reduction occurs with $E_{1/2}$ = −0.7 V *vs.* S.C.E. Hydrogen peroxide is probably formed.

The two following unsuccessful attempted chemical or electrochemical syntheses of (**6**) from fluorenone and succinonitrile emphasise the advantages of the electrochemical route described now. Condensation does not occur between FlC=O and succinonitrile under the conditions in ref. 14 which relate to the synthesis of $\mathrm{FlC(OH)CH_2CN}$ and FlC=CHCN from fluoren-9-one and acetonitrile in tetrahydrofuran as solvent. Similarly, condensation does not occur *via* the electrochemical route with succinonitrile–DMF (1 : 10) as solvent.

The dinitrile (**6**) is a pale brown powder: m.p. 156 °C (from chloroform–hexane); $\delta(\mathrm{CDCl_3})$: 3.9 (s, 2H), 7.0—7.7 (m, 7H), and 8.3—8.5 (m, 1H); i.r. (KBr) ν(CN) 2260w and 2210s cm^{-1}; *m/z* 242 ($M^{\cdot+}$, 100%). It has a half-wave reduction potential $E_{1/2}$ = −1.18 V *vs.* S.C.E. (DMF as solvent) at a rotating disc electrode.

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