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Evidence for the Transition from S_N to ET Mechanism in the Reaction of Arene Radical Anion with Alkyl Halide Evoked by the Introduction of an Electron Withdrawing Substituent into Radical Anion.

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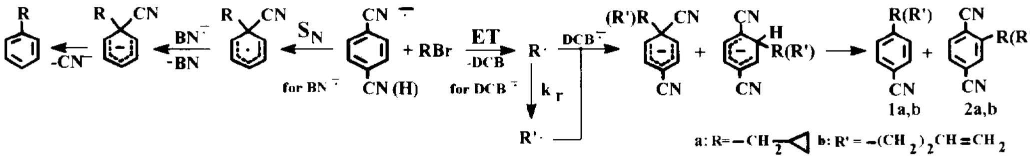
Abstract: The interaction of potassium salts of benzonitrile and 1,4-dicyanobenzene radical anions with cyclopropylmethyl bromide provides benzylcyclopropane, in the first case, and 4-alkyl- benzonitriles together with 2-alkyl-1,4-dicyanobenzenes containing both cyclopropylmethyl and it's isomeric 3-butenyl fragment, in the second case. These results provide evidence for the change of reaction mechanism from S_N to ET.

The investigation of factors governing nucleophilic substitution (S_N) and electron transfer (ET) competition in reactions of nucleophile + electrophile type is of paramount significance for the development of theoretical concepts in organic chemistry.[1] Stable arene radical anions occupy special position among nucleophiles owing to the orbital partition of nucleophilic and SET reductive functionalities.[2]

The S_N/ET ratio change has been reported earlier[3,4] in the reaction of arene radical anions with alkylating reagents concomitant with varying a substituent in electrophile as well as replacing a solvent. To the best of our knowledge, until now there were no clear examples of transition between S_N and ET as a prevailing mechanism upon the variation of substituent in a radical anion. In this connection we believe worth-while to report about the observation testifying in favour of this transition initiated by introducing substituent, particularly an electron withdrawing one such as cyano group, into an arene radical anion. To reveal this, the interactions of benzonitrile ($BN^{\cdot-}$) and 1,4-dicyanobenzene ($DCB^{\cdot-}$) radical anions with cyclopropylmethyl bromide as a testing reagent generating a fast rearranging alkyl radical in the course of ET process[5,6] have been investigated. The solutions of radical anions $BN^{\cdot-}$ and $DCB^{\cdot-}$ (cf. [8]) (concentrations 6×10^{-3}–9×10^{-3} M) were generated by potassium reduction of parent nitriles (BN was taken in 100 % and DCB in 5 %, because of its low solubility, excess to potassium) in liquid ammonia at -33 °C under argon atmosphere. Their stability is illustrated by the complete recovery of starting nitrile when the reduction products were brought into contact with air and by the fact that treatment of these solutions by water gives the 1:1 mixture of BN and benzene or DCB and BN that is in accordance with the protonation of radical anions at ipso-position (cf. [8b,c]).

The reaction of $BN^{\cdot-}$ provided benzylcyclopropane (yield 90 %).[9,10] No discernible amounts of compounds containing rearranged (3-butenyl) fragment have been formed. Unlike this the interaction of $DCB^{\cdot-}$ with testing reagent was characterized by less conversion and led to incorporation of alkyl fragment not only into *ipso*-, but also into *ortho*-position with the respect to cyano group providing compounds containing both cyclopropylmethyl radical -**1a** (18 %) and **2a** (9 %) and its isomeric 3-butenyl radical -**1b** (6 %) and **2b** (3 %),[11] the ratio n/i=(**1a**+**2a**)/(**1b**+**2b**)=3 (see scheme). The formation of compounds **1b** and **2b** as well as identical regioselectivity for cyclopropylmethyl and 3-butenyl radical incorporation - **1a**/**2a**=**1b**/**2b**=2 - allows the assignment of **1a,b** and **2a,b** to an ET mechanism.



Two competitive reaction pathways are conceivable for the initially formed cyclopropylmethyl radical (R·): rearrangement into 3-butenyl radical (R'·, $k_r = 5\times10^6\ s^{-1}$ at -33 °C [12]) and recombination with radical anion. The rate of latter processes is limited by diffusion. Taking into account statistic multiplicity of appearing radical pairs, $k_{max} = 1/4\ k_{diff} = 5\times10^9\ M^{-1}\ s^{-1}$ [13] for $\eta_{NH_3} = 0.26$ sP at -33 °C [14]. Substitution of indicated k_{max} and k_r values into equation from [5a] provides the minimum ~25 % portion of products with rearranged alkyl fragment, that is in exact coincidence with n/i=3 experimentally obtained in reaction of $DCB^{\cdot -}$. The absence of products with 3-butenyl fragment in the case of $BN^{\cdot -}$ cannot be explained on the basis of an ET mechanism and suggests the realization of an S_N mechanism.

Thus, the transition from $BN^{\cdot -}$ to $DCB^{\cdot -}$ leads likely to the change of predominate mechanism from S_N to ET in the reaction of an radical anion with primary alkyl bromides. As an addition of electron withdrawing CN group is expected to slow down the reactivity of an radical anion both as nucleophile and as electron donor, the change of predominant mechanism in favour of ET (see scheme) in the passage from $BN^{\cdot -}$ to $DCB^{\cdot -}$ suggests the S_N mechanism more retarded and, consequently, more sensible than ET one to this structural change.

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9. Product outcomes are related to theoretically possible one, the rest of mixture compounds were unreacted BN and DCB.
10. **Benzylcyclopropane** has been isolated by means of TLC. In its ^{1}H-NMR spectrum doublet at δ 2.5 ppm and multiplet in the area δ 0.1–1.5 ppm correspond to the cyclopropylmethyl fragment bonded to aromatic ring.
11. Individual compounds **1a, 2a, 1b** and mixture of **2a** and **2b** have been isolated by TLC. **4-Cyclopropylmethyl-benzonitrile (1a)**: ^{1}H-NMR, ($(CD_3)_2CO$, 90 MHz) δ 0.10–0.60 (m, 4H, 2CH_2), 0.6–1.2 (m, 1H, CH), 2.53 (d, 2H, CH_2), 7.35–7.60 (AB system, δ_A=7.39, δ_B=7.60, 4H, J_{AB}=8 Hz); IR, (cm^{-1}) 2230 (C≡N); Calcd. for $C_{11}H_{11}N$: 157.0891. Found: 157.0892. **2-Cyclopropylmethyl-1,4-dicyanobenzene (2a)**: ^{1}H-NMR, ($(CD_3)_2CO$, 200 MHz) δ 0.25–1.20 (m, 5H, C_3H_5), 2.77 (d, 2H, CH_2), 7.84 (dd, 1H, J=8, 1.5 Hz, 5-H), 7.96 (d, 1H, J=8 Hz, 6-H), 8.03 (s, 1H, 3-H); IR, (KBr, cm^{-1}) 2235, 2240 (2 C≡N); Calcd. for $C_{12}H_{10}N_2$: 182.0844. Found: 182.0847. **(3-Butenyl)-benzonitrile (1b)**: ^{1}H-NMR ($(CD_3)_2CO$, 60 MHz) δ 2.43 (t, 2H, J=7 Hz, α-CH_2), 2.73 (q, 2H, J=7 Hz, β-CH_2), 4.80–5.00 (m, 2H, H_2C=), 5.82–6.67 (m, 1H, -CH=), 7.30–7.72 (AB system, δ_A=7.40, δ_B=7.62, 4H, J_{AB}=8 Hz); IR, (cm^{-1}) 2230 (C≡N); Calcd. for $C_{11}H_{11}N$: 157.0891. Found: 157.0906. **(3-Butenyl)-1,4-dicyanobenzene (2b)**: ^{1}H-NMR ($(CD_3)_2CO$, 90 MHz) δ 2.42 (m 2H, α-CH_2), 2.94 (m 2H, β-CH_2), 4.82–5.04 (m, 2H, H_2C=), 5.56–6.20 (m, 1H, =CH-), 7.71–7.90 (m 3H, 3-H, 5-H and 6-H).
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