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SIMULTANEOUS OCCURRENCE OF ELECTRON TRANSFER INITIATED RADICAL CAGE COLLAPSE AND CHAIN MECHANISMS IN THE REACTIONS OF DIARYLIODONIUM CATIONS WITH 2-NITROPROPANATE ANION

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Summary: Simultaneous occurrence of free radical cage and chain mechanisms initiated by single electron transfer in the reactions of diaryliodonium cations with 2-nitropropanate anion has been established.

Intervention of radicals in the reactions of arenediazonium salts with certain anions has been satisfactorily explained in terms of single electron transfer pathways;[1-3] but the mode of initiation and bond reorganization in the free radical reactions[4,5] of diaryliodonium cations 1 with anions is poorly understood.[6] We now report simultaneous occurrence of electron transfer initiated radical cage and chain mechanisms in the reactions of three diaryliodonium cations viz., $Ph-\overset{+}{I}-Ph$ 1a, $p-Me-C_6H_4-\overset{+}{I}-Ph$ 1b, and $p-MeO-C_6H_4-\overset{+}{I}-Ph$ 1c, with 2-nitropropanate anion 2.

On reacting 5×10^{-3} mol of diaryliodonium bromide with lithium 2-nitropropan-2-ide,[7] in absolute methanol at 30°C under varying conditions, the product distribution listed in the Table was obtained. It is evident from run 4 (in presence of α-methylstyrene) that the formation of arylated nitroparaffins on one hand and benzene, toluene, anisole, biaryls and formaldehyde on the other, takes place by two competing pathways. The possibility of occurrence of an S_NAr process leading to arylated nitroparaffins is ruled out since nitronic esters, or products derived therefrom were not obtained in these reactions.[8] Furthermore, the ratios of arylated nitroparaffins 7 and 8 obtained in runs 6 and 8, respectively, do not conform to the formation of these products by an S_NAr process.[9] Our inability to detect any 2-(m-tolyl)-2-nitropropane or 2-(m-anisyl)-2-nitropropane among the products in the reactions of 1b and 1c, inspite of careful search, clearly eliminates the possibility of existence of aryne intermediates. These arguments coupled with the observation concerning catalysis by light and inhibition by oxygen, indicate effective intervention of radicals in these reactions.

In view of the known function of diaryliodonium cations as electron acceptors[10] under suitable conditions and that of the 2-nitropropanate anion as an electron donor towards comparatively weaker acceptors,[7,11] we propose that the

TABLE: Reactions[a] of 1 with Lithium-2-nitropropan-2-ide in Methanol at 30°C

Run	Diaryl-iodo-nium bromide 1	Atmos-phere	Time (hr)	% Yield of Products[b]									
				Ph-H	Ar-H	$PhCMe_2NO_2$	$ArCMe_2NO_2$	Ph-I	Ar-I	Biaryls	O_2NMe_2C- O_2NMe_2C[c]	CH_2O[d]	Starting Material 1[e]
1	1a	Nitrogen	48	43	-	41	-	94	-	5	5	38	-
2	1a	Oxygen[f]	96	5	-	6	-	18	-	-	-	-	80
3[g]	1a	Nitrogen	48	38	-	22	-	70	-	3	2	32	30
4[h]	1a	Nitrogen	48	8	-	67	-	88	-	2	2	-	10
5[i]	1a	Nitrogen	48	38	-	36	-	87	-	4	4	33	10
6	1b	Nitrogen	48	23	21	24	16	44	54	5[j]	6	37	-
7	1b	Oxygen[f]	96	4	4	3	2	8	10	-	-	-	80
8	1c	Nitrogen	48	23	18	28	13	38	57	6[k]	5	35	-
9	1c	Oxygen[f]	96	4	4	2	2	6	8	-	-	-	85

a. Unless otherwise stated, 5 x 10^{-3} mol of diaryliodonium bromide was reacted with lithium 2-nitropropan-2-ide (0.1 mol) under laboratory lights.

b. Percentages based on diaryliodonium bromide unless otherwise stated. Phenol 9%, 4% and 5% was also obtained in runs 2, 7 and 9 respectively, besides p-cresol 4% in run 7 and p-methoxyphenol 4% in run 9.

c. Percentage based on lithium 2-nitropropan-2-ide. d. Estimated as dimedone derivative. e. Recovered and estimated as diaryliodonium iodide.

f. Oxygen was bubbled through the reaction mixture.

g. With 5 x 10^{-3} mol of lithium 2-nitropropan-2-ide.

h. In presence of α-methylstyrene (0.01 mol); i. In dark.

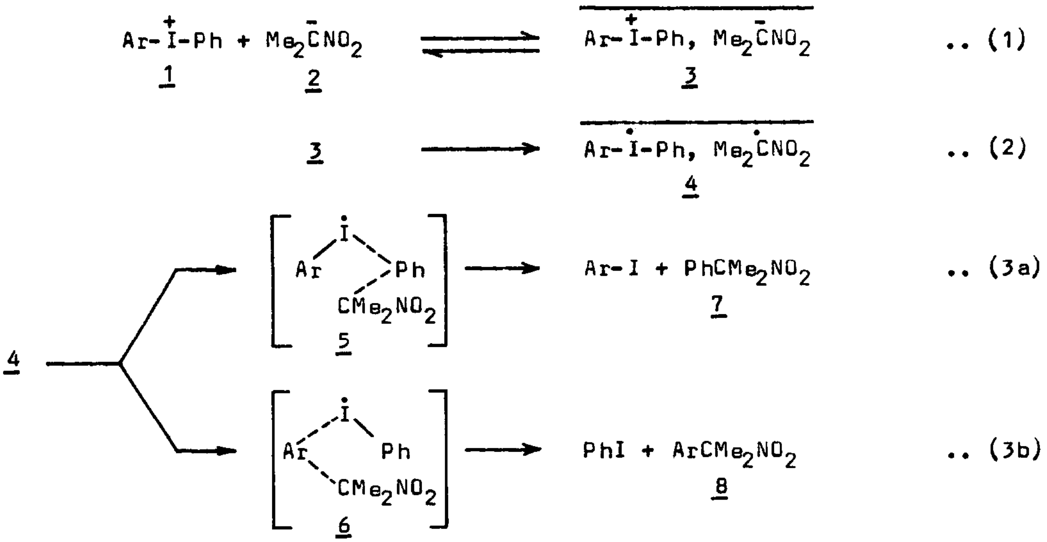
j. Biphenyl (3%), di-p-tolyl (2%) and a trace of p-methylbiphenyl.

k. Biphenyl (3%), di-p-anisyl (3%), and a trace of p-methoxybiphenyl.

electron transfer process outlined in Scheme I, accounts for the major portions of products 7 and 8 in addition to iodoarenes. The reversibility of step (1) is established by a comparison of the product distributions obtained in runs 1 and 3.[12] The radical pair 4 is obtained from the ion pair 3 by an electron transfer process. The decomposition of 4 in the solvent cage yields 7 and 8. The fact that product ratios in similar radical reactions of aryliodonium salts with different anions are dependent on the nature of the reductant[4] indicates that the transition state for the collapse of 4 must involve both the radical species present. Thus, transition states resembling 5 and 6 could be visualized for the formation of 7 and 8, respectively.

The development of a low energy transition state would be favoured by the lengthening of the energetically weaker C-I bond during the homolysis of p-R-C_6H_4-$\dot{I}$-Ph and spin pairing to a significant extent between the odd elec-

SCHEME I



trons of the incipient aryl radical and the relatively stable 2-nitropropyl radical in the solvent cage. As the bond dissociation energies of aryl carbon-iodine bond in homolysis follow the order: $Ph\text{-} < p\text{-}Me\text{-}C_6H_4\text{-} < p\text{-}MeO\text{-}C_6H_4\text{-}$,[5,13] the transition state in the reactions of 1b and 1c would resemble 5 more than 6. This accounts for the ratios of the products 7 and 8 actually observed in runs 6 and 8.

The radicals escaping from the cage, 4, initiate a concurrent chain process outlined in Scheme II and thus, account for the remaining products.

SCHEME II

Initiation: $\overline{\mathrm{Ar\text{-}\dot{I}\text{-}Ph,\ Me_2\dot{C}NO_2}} \longrightarrow (\mathrm{Ar^{\bullet} + Ph\text{-}I})$ or $(\mathrm{Ph^{\bullet} + Ar\text{-}I}) + \mathrm{Me_2\dot{C}NO_2}$

Propagation: $\mathrm{Ar^{\bullet}}$ (or $\mathrm{Ph^{\bullet}}$) $+ \mathrm{CH_3OH} \longrightarrow \mathrm{Ar\text{-}H}$ (or $\mathrm{Ph\text{-}H}$) $+ \mathrm{{}^{\bullet}CH_2OH}$

$$\underset{\underline{1}}{\mathrm{Ar\text{-}\overset{+}{I}\text{-}Ph}} + \mathrm{{}^{\bullet}CH_2OH} \longrightarrow \underset{\underline{9}}{\mathrm{Ar\text{-}\dot{I}\text{-}Ph}} + \mathrm{{}^{+}CH_2OH}$$

$$\mathrm{Ar\text{-}I} + \underset{\underline{10}}{\mathrm{Ph^{\bullet}}} \longleftarrow \underline{9} \longrightarrow \underset{\underline{11}}{\mathrm{Ar^{\bullet}}} + \mathrm{Ph\text{-}I};\quad \mathrm{{}^{+}CH_2OH} \longrightarrow \mathrm{CH_2O} + \mathrm{H^{+}}$$

Termination: $\mathrm{Ar^{\bullet}}$ (or $\mathrm{Ph^{\bullet}}$) $+ \mathrm{Ar\text{-}H} \xrightarrow{-\mathrm{H^{\bullet}}} \mathrm{Ar\text{-}Ar}$ (or $\mathrm{Ar\text{-}Ph}$)

$\mathrm{Ar^{\bullet}}$ (or $\mathrm{Ph^{\bullet}}$) $+ \mathrm{Ph\text{-}H} \xrightarrow{-\mathrm{H^{\bullet}}} \mathrm{Ar\text{-}Ph}$ (or $\mathrm{Ph\text{-}Ph}$)

$2\mathrm{Ar^{\bullet}} \longrightarrow \mathrm{Ar\text{-}Ar}$; $2\,\mathrm{Ph^{\bullet}} \longrightarrow \mathrm{Ph\text{-}Ph}$; $\mathrm{Ar^{\bullet}} + \mathrm{Ph^{\bullet}} \longrightarrow \mathrm{Ar\text{-}Ph}$

$2\,\mathrm{Me_2\dot{C}NO_2} \longrightarrow \mathrm{O_2NMe_2C\text{-}CMe_2NO_2}$

$\mathrm{Ar^{\bullet}}$ (or $\mathrm{Ph^{\bullet}}$) $+ \mathrm{Me_2\dot{C}NO_2} \longrightarrow \mathrm{Ar\text{-}CMe_2NO_2}$ (or $\mathrm{Ph\text{-}CMe_2NO_2}$)

The chain is propagated by a hydrogen atom abstraction from methanol giving hydroxymethyl radical and subsequent electron transfer from $^{\bullet}CH_2OH$ to the diaryliodonium cation 1. Such a process is precedented in the reactions of arenediazonium salts in methanol medium.[1,2] The ratio of the products: benzene/anisole in run 8 is consistent with the relative concentrations of 10 and 11 as produced from 9 in the reported[10] reduction of 1c with Ti(III).

Though α-methylstyrene effectively inhibits the chain mechanism, by scavenging the free aryl radicals, it is known not to significantly effect the cage processes.[14] Indeed, in its presence more of the reaction in run 4 proceeds by the radical cage process shown in Scheme I, leading to an increase in the yield of 2-phenyl-2-nitropropane. Oxygen inhibits the free radical chain pathway and also interferes with the cage mechanism.[15]

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REFERENCES AND NOTES

(1) Ramesh Kumar and P.R. Singh, Tetrahedron Lett., 613 (1972).
(2) P.R. Singh and Ramesh Kumar, Austral. J. Chem., 25, 2133 (1972).
(3) P.R. Singh, B. Jayaraman and H.K. Singh, Chem. and Ind., 311 (1977).
(4) F.M. Beringer and R.A. Falk, J. Chem. Soc., 4442 (1964).
(5) J.L. Lubinkowski, L.C. Arrieche and W.E. McEwen, J. Org. Chem., 45, 2076 (1980) and references cited therein.
(6) P.R. Singh and R.K. Khanna, Handbook, 3rd International Symposium on free radicals, Freiburg, West Germany, 1981, pp. 234.
(7) R. Kerber, G. Urry and N. Kornblum, J. Am. Chem. Soc., 86, 3904 (1964).
(8) B. Bigot, D. Roux and L. Salem, J. Am. Chem. Soc., 103, 5271 (1981).
(9) C.C. Lai and W.E. McEwen, Tetrahedron Lett., 3271 (1971).
(10) F.M. Beringer and P. Bodlaender, J. Org. Chem., 34, 1981 (1969).
(11) N. Kornblum and M.J. Fifolt, J. Org. Chem., 45, 360 (1980).
(12) Equilibrium is shifted to the right with increasing amounts of 2, leading to an enhancement in the yields of products derived from ion pairs.
(13) F.M. Beringer and I. Lillien, J. Am. Chem. Soc., 82, 5135 (1960).
(14) T. Holm and I. Crossland, Acta Chem. Scand., B33, 421 (1979).
(15) Though 2-nitropropanate anion is stable to oxygen, in presence of radicals it reacts to yield NO_2^- and acetone by a chain process. See, G.A. Russell and W.C. Danen, J. Am. Chem. Soc., 88, 5663 (1966).

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