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BRIDGED RADICALS IN THE REACTION OF SODIUM DIHYDRONAPHTHYLIDE WITH GEM-DICHLORIDES

P.R. SINGH and B. JAYARAMAN
Department of Chemistry
Indian Institute of Technology, Kanpur, India

The reactions of sodium dihydronaphthylide with dichlorodiphenylmethane and 9,9-dichlorofluorene in THF at 0°C have been found to proceed by an electron transfer mechanism involving α-chloro radicals, vicinal-dichlorides and an equilibrating pair of classical and bridged β-chloro radicals.

In recent years, it has been established that on reaction with sodium dihydronaphthylide ($Na^+C_{10}H_8^{\dot{-}}$), several alkyl[1-5] and aryl[6-9] halides (R-X) undergo electron transfer reduction leading to the cleavage of carbon-halogen bonds. The resultant radicals R· act as precursor of the products R-H, R-R and alkyl- or arylnaphthalenes. While the mechanistic details concerning these reactions are well understood, reports on the reaction of $Na^+C_{10}H_8^{\dot{-}}$ with gem-dihalides are scanty. Sargent[10] has postulated the intermediacy of a carbene radical-anion in the reaction of $Na^+C_{10}H_8^{\dot{-}}$ with 2,2-dichloro-3,3-dimethylbutane; but the existence of such a species in reactions with other gem-dihalides remains to be tested.

We have examined the reactions of $Na^+C_{10}H_8^{\dot{-}}$ with dichlorodiphenylmethane (Ia) and 9,9-dichlorofluorene (Ib). The results obtained under different conditions are recorded in Table 1. The green color of $Na^+C_{10}H_8^{\dot{-}}$ disappeared immediately after the addition of its THF solution to that of Ia, but persisted for a few seconds in the case of Ib. The reaction mixtures were worked up after continuous magnetic stirring for 15 min at 0°C and products isolated by either fractional crystallization or chromatography over silica-gel column using petroleum ether (bp 60-80°C) and petroleum ether (bp 60-80°C)-benzene mixtures as eluents. Substantial quantities of pasty materials also produced in each experiment could not be analysed. The isolated products were characterized by elemental analyses and comparison with authentic samples (ir spectra, tlc and mixed mp).

Table I: Reaction of *gem*-Dichlorides (0.005 mol) with $Na^{+}C_{10}H_{8}^{\dot{-}}$ in 30 ml THF at 0°C

Dichloride (I)	Ratio of I to $Na^{+}C_{10}H_{8}^{\dot{-}}$	Reaction atmosphere	Products (% yield*)
Ia	1:2	N_2	Tetraphenylethylene (60%)
Ia	1:2	Air	Tetraphenylethylene (38%) Tetraphenylethylene oxide (20%)
Ia	1:2	N_2 and cyclohexene (0.15 mol)	Tetraphenylethylene (26%) 1,1,2,2-Tetraphenylethane (28%)
Ia	1:1	N_2 and cyclohexene (0.15 mol)	Tetraphenylethylene (16%) 1,1,2,2-Tetraphenylethane (16%) Ia (40%)
Ib	1:2	N_2	Bifluorenylidene (50%) 9,9'-Dichloro-9,9'-bifluorenyl (12%) Fluorene (5%)
Ib	1:2	N_2 and cyclohexene (0.15 mol)	Bifluorenylidene (44%) 9,9'-Dichloro-9,9'-bifluorenyl (12%) Fluorene (9%)
Ib	1:1	N_2	Bifluorenylidene (28%) 9,9'-Dichloro-9,9'-bifluorenyl (7%) Ib (46%)

*The yields are averages of best three experiments.

The formation of tetraphenylethylene in all the experiments involving Ia and that of bifluorenylidene in reactions of Ib coupled with other observations recorded in Table 1 and elsewhere in the literature suggests that the mechanistic sequence outlined in Scheme 1 represents a major component in the over-all reactions:

Scheme 1

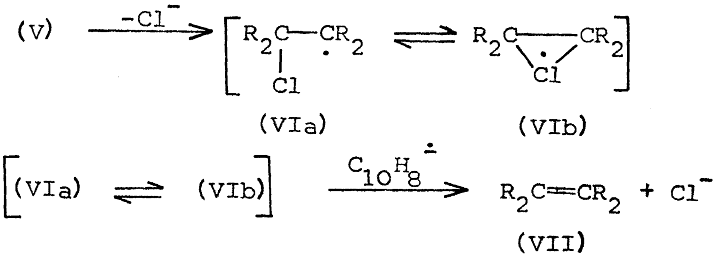
$$\underset{\text{(I)}}{R_2CCl_2} \xrightarrow{C_{10}H_8^{\dot{-}}} \underset{\text{(II)}}{R_2CCl_2^{\dot{-}}} \xrightarrow{-Cl^{-}} \underset{\text{(III)}}{R_2\dot{C}\text{-}Cl} \qquad (1)$$

$$\text{(III)} \xrightarrow{\text{dimerization}} \underset{\text{(IV)}}{R_2C(Cl)\text{-}C(Cl)R_2} \qquad (2)$$

$$\text{(IV)} \xrightarrow{C_{10}H_8^{\dot{-}}} \underset{\text{(V)}}{R_2C(Cl)\text{-}C(Cl)R_2^{\dot{-}}} \qquad (3)$$

contd.

Scheme 1 (contd.)



(4)

(5)

From a knowledge of the known reactions of $\mathrm{Na^+C_{10}H_8^{\dot{-}}}$ with alkyl- and aryl-halides, it is concluded that the formation of α-chloro radical (III) via reductive dechlorination of I constitutes the first step of fundamental importance. While III readily dimerizes to produce vicinal-dichloride (IV), it does not prefer hydrogen atom abstraction from the solvent. The latter argument is supported by the total absence of diphenylmethyl chloride and 9-chlorofluorene among the products of the reactions of Ia and Ib respectively. Similar behaviour has been recently observed$^{11)}$ for diphenylmethyl and 9-fluorenyl radicals. The possibility of formation of α-chloro carbanions by the reduction of III is ignored because we failed to trap any of these carbanions by the Bank's anion trapping technique.$^{4,9)}$

The dichloride (IV) undergoes reductive dechlorination$^{12)}$ via electron transfer to give β-chloro radical (VIa) which rapidly equilibrates with the bridged radical (VIb).$^{13)}$ On further reduction with $\mathrm{C_{10}H_8^{\dot{-}}}$, (VIa) and (VIb) both yield the olefinic compound (VII). That IV effectively competes with I for $\mathrm{Na^+C_{10}H_8^{\dot{-}}}$ without the likelihood of its being converted into the latter halide is established on the basis of results recorded in Table 2.

Table 2: Reaction of 1,2-Dichlorotetraphenylethane (A) with $\mathrm{Na^+C_{10}H_8^{\dot{-}}}$ in 30 ml THF at 0°C

Mole of (A)	Mole of $\mathrm{Na^+C_{10}H_8^{\dot{-}}}$	Reaction atmosphere	Products (% yield*)
0.0025	0.005	N_2 and Ia (0.0025 mol)	Tetraphenylethylene (62% of A) Ia (96% of original)
0.0025	0.005	N_2, Ia (0.0025 mol) and cyclohexene (0.15 mol)	Tetraphenylethylene (30% of A) 1,1,2,2-Tetraphenylethane(31% of A) Ia (95% of original)
0.005	0.01	N_2	Tetraphenylethylene (76%)
0.005	0.01	N_2 and cyclohexene (0.15 mol)	Tetraphenylethylene (35%) 1,1,2,2-Tetraphenylethane (39%)

*The yields are averages of best three experiments. Pasty materials obtained in each experiment could not be analysed.

Formation of substantial amount of tetraphenylethylene oxide when the reaction of Ia is conducted in air could be rationalized assuming that III reacts with paramagnetic O_2.

Isolation of IV in the reaction of Ib but not in the case of Ia indicates faster consumption of 1,2-dichlorotetraphenylethane as compared to 9,9'-dichloro-9,9'-bifluorenyl. This is consistent with the marginally slower disappearance of the green color of $Na^+C_{10}H_8^{\dot{-}}$ in its reaction with Ib relative to Ia particularly when the ratios of the concentrations of gem-dichloride to $Na^+C_{10}H_8^{\dot{-}}$ were 1:2.

The increased yield of fluorene in the reaction of Ib in presence of an excess of cyclohexene indicates the ease with which the latter donates its allylic hydrogen atom to radicals. While no 9,9'-bifluorenyl is isolated in this reaction, a substantial quantity of 1,1,2,2-tetraphenylethane is produced at the expense of tetraphenylethylene in that involving Ia. Presumably, the equilibrium (VIa) $\rightleftharpoons$ (VIb) in the former reaction is far to the right and VIb upon reduction with $Na^+C_{10}H_8^{\dot{-}}$ collapses to VII without having a chance to abstract hydrogen from cyclohexene; but in the latter, VIa is present in significantly larger concentration to abstract hydrogen eventually producing 1,1,2,2-tetraphenylethane.

The intervention of carbene and carbene radical-anion intermediates is ruled out because we failed to detect any carbene addition/insertion products with cyclohexene inspite of a careful search. Further experiments designed to evaluate the proposed mechanism are in progress and will be reported later.

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