Tetrahedron Letters No. 51, pp 4685-4686, 1976. Pergamon Press. Printed in Great Britain.

EVIDENCE FOR AN ELECTRON TRANSFER MECHANISM IN THE COUPLING OF CYCLOPROPENYL CATIONS WITH CYCLOPROPENYL ANIONS

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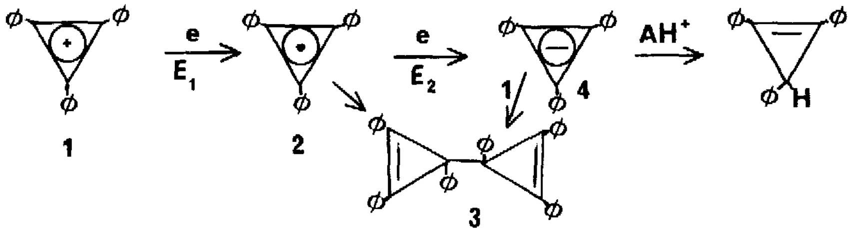
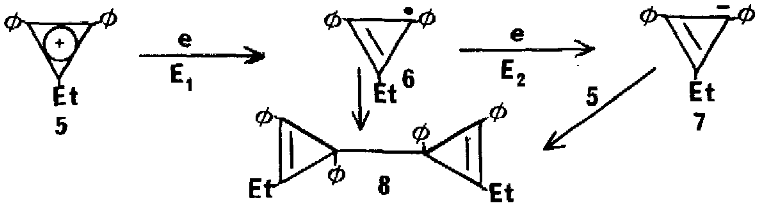
(Received in USA 23 September 1976; received in UK for publication 11 November 1976)

We have described[1,2,3] the generation of various cyclopropenyl radicals and anions by electrochemical reduction of the corresponding cations. For instance, triphenylcyclopropenyl cation (1) could be reduced at E_1 to radical 2 which dimerized to hexaphenyl-bis-cyclopropenyl (3) quantitatively. Cyclopropenyl anion 4, generated at E_2, was captured by 1 to afford the same dimer, although it could also be trapped by protonation.[2]

Capture of 4 by 1 was much more effective than capture by protonation with guanidinium cation, so that only 12% of triphenylcyclopropene was formed at potentials beyond E_2 even though guanidinium cation was in one-hundred-fold excess over 1.[2] We suggested that the very effective trapping of a cyclopropenyl anion by a cyclopropenyl cation proceeds by an electron transfer, with large collision cross-section, followed by coupling of the resulting radicals. We now wish to report evidence which supports this mechanism of anion-cation coupling.

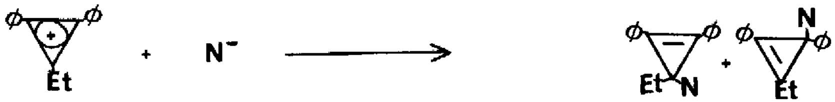


2,3-Diphenylethylcyclopropenyl perchlorate[4] (5) shows polarographic waves in CH_3CN at -0.84V(E_1) and -1.98V(E_2) vs. s.c.e. Preparative reduction of 3 at E_1 affords the dimer 8 in which coupling has occurred at a phenylated carbon, as we had reported earlier[4] for Zn reduction of 5 fluoroborate. The same dimer 8 is formed as the only detectable isomer, in 73% isolated yield, when 5 is electrolyzed at -2.3V, well beyond E_2, to form 7.



This is the result expected if 7 reacts with 5 by prior electron transfer to afford a pair of cyclopropenyl radicals (6). These couple to afford 8, as we observe also at E_1, because the transition state prefers to localize the odd electron on a phenylated carbon. However, a simple nucleophilic addition of an anion such as 7 to 5 should occur to some extent at the ethylated carbon of 5, the best place[5] to localize positive charge. With other nucleophiles such addition to 5 is either predominant or at least significant, as Table 1 indicates.

TABLE 1



REAGENT	N^-	SOLVENT	PRODUCT RATIO	
CH_3Li	CH_3^-	Et_2O	67	33
CH_3MgI	CH_3^-	Et_2O	80	20
		DME	67	33
ϕCH_2MgCl	ϕCH_2^-	Et_2O	55	45
		DME	25	75
$LiAlH_4$	H^-	Et_2O	95	<5
		DME	95	<5
$(CH_3)_2CuLi$	CH_3^-	Et_2O	80	20
		DME	75	25

DME: dimethoxyethane Et_2O: diethyl ether

In all these cases nucleophilic attack is predominant at the ethylated carbon of 5, except for reaction with benzylmagnesium iodide in dimethoxyethane in which it is still easily detectable (product analysis by nmr). It is striking that methylation with lithium dimethyl cuprate also occurs at the ethylated carbon of 3, although House's work[6] indicates that this should proceed by electron transfer from cuprate to generate radical 6. Of course 6 could then react with the copper before methyl transfer occurs.

We have reported previously[7] another example in which addition to an unsymmetrical cyclopropenyl cation occurred at a different carbon from that added to in the corresponding cyclopropenyl radical, in accord with expected substituent effects on the localized transition states. The current work shows that such effects can be used to decide the precise timing of electron and nuclear motions in an overall nucleophilic addition. It also confirms our previous suggestion that the electron transfer mechanism may explain the remarkable effectiveness of cyclopropenyl cations in trapping cyclopropenyl anions.

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