

## Hypovalent Radicals. Chemical Trapping of Electrogenerated Diazoalkane Anion Radicals

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**Summary** Diazoalkane anion radicals produced by electroreduction of diazodiphenylmethane ( $\text{Ph}_2\text{CN}_2$ ) and 9-diazo fluorene ( $\text{FlN}_2$ ) in the presence of certain proton donors yield the corresponding hydrazones ( $\text{R}_2\text{C}=\text{NNH}_2$ ); formation of diphenylmethane from electroreduction of  $\text{Ph}_2\text{CN}_2$  is shown to proceed by formation of the carbene anion radical  $\text{Ph}_2\text{C}^{\cdot-}$ .

$[(\text{R}_2\text{C}=\text{N})_2]$  involving  $\text{R}_2\text{CH}^-$  as the initiator and  $\text{R}_2\text{CN}_2^{\cdot-}$  as the chain carrying species. This prompts us to report that electroreductions of diazodiphenylmethane ( $\text{Ph}_2\text{CN}_2$ ) and 9-diazo fluorene ( $\text{FlN}_2$ ) in the presence of proton donors trap the diazoalkane anion radicals ( $\text{R}_2\text{CN}_2^{\cdot-}$ ) yielding the hydrazones ( $\text{R}_2\text{C}=\text{NNH}_2$ ), and that the other major product from  $\text{Ph}_2\text{CN}_2$ ,  $\text{Ph}_2\text{CH}_2$ , is produced exclusively *via* the carbene anion radical,  $\text{Ph}_2\text{C}^{\cdot-}$ .

BETHELL *et al.*<sup>1</sup> recently published results suggesting a new chain reaction for the conversion of  $\text{R}_2\text{CN}_2$  into azines

Using h.p.l.c. rather than g.p.c. to analyse the products from controlled potential electrolytic reductions of

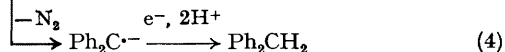
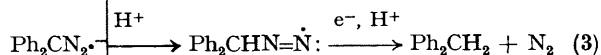
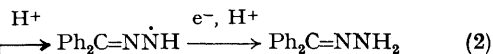
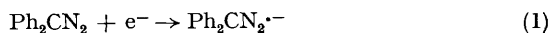
TABLE. Product studies of the controlled-potential, electrolytic reductions of diazodiphenylmethane and diazofluorene.<sup>a</sup>

Run	Cmpd. (conc./mM)	[DEM]/ mM	$E_{app}/$ V	$n$	% Yield of products						
					$R_2C=N-N=CR_2$	$R_2CH_2$	$R_2C=O$	$R_2C=NNH_2$	$NNHCHR_2$	$R_2CN_2$	$R_2CH_2/R_2C=NNH_2$
1	$Ph_2CN_2$ (4.53)	0	-1.20	0.40	78	5	0.8	0.6	2.2	5	8
2	$Ph_2CN_2$ (4.54)	39	-1.10	2.00	0.7	85	1.0	7.6	3.0	2.4	11
3	$Ph_2CN_2$ (3.02) <sup>b</sup>	32	-1.20	2.45	1.3	44	2.6	21	2.7	18	2
4	$Ph_2CN_2$ (1.40) <sup>b</sup>	143	-1.20	2.00	0.3	34	— <sup>c</sup>	37	2.5	24	0.9
5	$FlN_2$ (3.37)	0	-0.53	0.16	97	1.0	0.5	trace	— <sup>c</sup>	2.7	—
6	$FlN_2$ (3.27)	20	-0.57	0.50	73	0.6	8	14	— <sup>c</sup>	3.1	0.04

<sup>a</sup> Reductions were effected at a platinum cathode in DMF-0.1 F  $Bu^n_4NClO_4$  at room temperature (20–23 °C); potentials are with respect to a cadmium amalgam reference electrode which is saturated with respect to NaCl and  $CdCl_2$  in DMF. <sup>b</sup> Reduction effected at 0 °C. <sup>c</sup> Not detected.

$Ph_2CN_2$  and  $FlN_2$  (dimethylformamide-0.1 F  $Bu^n_4NClO_4$  at platinum electrodes),<sup>2,3</sup> small, but discernible, amounts of simple hydrazones,  $R_2C=NNH_2$ , were observed as products (runs 1 and 5, Table). Control experiments demonstrated that these hydrazones were not produced from the other nitrogen-containing products upon electroreduction at the applied potential.

In order to establish a plausible mechanism by which these hydrazones are produced, the electroreductions of the two diazoalkanes were carried out in the presence of numerous proton donors including electro-inactive diethyl malonate (DEM). These results (compare run 1 with runs 2–4) show that the addition of DEM to the electrolysis solution of  $Ph_2CN_2$  causes significant increases in the yields of  $Ph_2CH_2$  and  $Ph_2C=NNH_2$  and a concomitant decrease in the yield of benzophenone azine ( $Ph_2C=N-N=CPh_2$ ). More importantly, the  $Ph_2CH_2/Ph_2C=NNH_2$  product ratio decreases with both increasing concentration of DEM and decreasing temperature (runs 2–4). These results are clearly inconsistent with ambident behaviour of  $Ph_2CN_2^{\cdot-}$  towards protonation as the only source of  $Ph_2CH_2$  (equations 3, 4). We consider that the other intermediate leading to  $Ph_2CH_2$  is  $Ph_2C^{\cdot-}$ .



Cyclic voltammetric studies of the reduction of  $Ph_2CN_2$  at 0 °C show  $Ph_2CH^{\cdot-}$  to be the only oxidizable intermediate

at scan rates in excess of 10 V s<sup>-1</sup>. As the scan rate is decreased, the following sequence of kinetically linked intermediates is observed:  $Ph_2CH^{\cdot-} \rightarrow Ph_2CHN=N=CPh_2^{\cdot-} \rightarrow Ph_2C=N-N=CPh_2^{\cdot-}$ . These observations specifically exclude  $Ph_2CN_2^{\cdot-}$ ,  $Ph_2CN_2H^{\cdot}$ ,  $Ph_2C^{\cdot-}$ , and  $Ph_2CH^{\cdot}$  as the first species to react with  $Ph_2CN_2$  in the formation of the azine.<sup>4</sup> This point and the above chemical trapping results require that formation of  $Ph_2C^{\cdot-}$  is a major reaction channel in product formation.

Electroreduction of  $FlN_2$  in the presence of DEM produced  $Fl=NNH_2$  and the azine ( $Fl=N$ )<sub>2</sub> (run 6). Subsequent control experiments demonstrated that  $Fl=NNH^{\cdot-}$  is only slowly protonated by DEM and that it reacts rapidly with  $FlN_2$  to form the azine.<sup>4</sup> Proton donors which protonate  $Fl=NNH^{\cdot-}$  rapidly are also electroactive and cannot be used with these electrochemical methods. However, the fact that the yield of  $Fl=NNH_2$  was significantly increased in the presence of DEM with no change in the yield of  $FlH_2$  strongly suggests that  $FlN_2^{\cdot-}$  does not function as an ambident species towards reaction with DEM. The planar structure and stabilization of the anion radical by the 9-fluorenylidene ring system should emphasize such ambident behaviour at C-9 of  $FlN_2^{\cdot-}$ . With  $Ph_2CN_2^{\cdot-}$ , steric and electronic factors disfavour protonation at C- $\alpha$  compared with  $FlN_2^{\cdot-}$ . Since proton transfer involves lower activation barriers than most other reactions, e.g. hydrogen atom abstraction, we believe that both  $Ph_2CN_2^{\cdot-}$  and  $FlN_2^{\cdot-}$  react only at the terminal nitrogen. Thus, the sole precursor to  $Ph_2CH_2$  from electroreduction of  $Ph_2CN_2$  is  $Ph_2C^{\cdot-}$ .<sup>5</sup>

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<sup>2</sup> R. N. McDonald, R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1977, **99**, 1268.

<sup>3</sup> R. N. McDonald, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1978, **100**, 995.

<sup>4</sup> R. N. McDonald, F. M. Triebe, and M. D. Hawley, unpublished results.

<sup>5</sup> R. N. McDonald, A. K. Chowdhury, and D. W. Setser, *J. Am. Chem. Soc.*, in the press; results of the gas-phase chemistry of cyclopentadienyldiene anion radical have established that the principal reaction channel of the carbene anion radical with the diazo compound is formation of the corresponding azine anion radical.