Hypovalent Radicals. Chemical Trapping of Electrogenerated Diazoalkane Anion Radicals

By F. M. TRIEBE, M. DALE HAWLEY,* and RICHARD N. McDONALD*
(*Department of Chemistry, Kansas State University, Manhattan, Kansas* 66506)

Summary Diazoalkane anion radicals produced by electroreduction of diazodiphenylmethane (Ph_2CN_2) and 9-diazofluorene (FlN_2) in the presence of certain proton donors yield the corresponding hydrazones ($R_2C{=}NNH_2$); formation of diphenylmethane from electroreduction of Ph_2CN_2 is shown to proceed by formation of the carbene anion radical $Ph_2C^{\cdot -}$.

BETHELL *et al.*[1] recently published results suggesting a new chain reaction for the conversion of R_2CN_2 into azines [$(R_2C{=}N{-})_2$] involving R_2CH^- as the initiator and $R_2CN_2^{\cdot -}$ as the chain carrying species. This prompts us to report that electroreductions of diazodiphenylmethane (Ph_2CN_2) and 9-diazofluorene (FlN_2) in the presence of proton donors trap the diazoalkane anion radicals ($R_2CN_2^{\cdot -}$) yielding the hydrazones ($R_2C{=}NNH_2$), and that the other major product from Ph_2CN_2, Ph_2CH_2, is produced exclusively *via* the carbene anion radical, $Ph_2C^{\cdot -}$.

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.[a]

Run	Cmpd. (conc./mM)	[DEM]/ mM	E_{app}/ V	n	% Yield of products $R_2C{=}N{-}N{=}CR_2$	R_2CH_2	$R_2C{=}O$	$R_2C{=}NNH_2$	$R_2C{=}NNHCHR_2$	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)[b]	32	−1·20	2·45	1·3	44	2·6	21	2·7	18	2
4	Ph_2CN_2(1·40)[b]	143	−1·20	2·00	0·3	34	—[c]	37	2·5	24	0·9
5	FlN_2(3·37)	0	−0·53	0·16	97	1·0	0·5	trace	—[c]	2·7	—
6	FlN_2(3·27)	20	−0·57	0·50	73	0·6	8	14	—[c]	3·1	0·04

[a] 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. [b] Reduction effected at 0 °C. [c] Not detected.

Ph_2CN_2 and FlN_2 (dimethylformamide–0·1 F $Bu^n{}_4NClO_4$ at platinum electrodes),[2,3] 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 $Ph_2C^{\cdot-}$.

$$Ph_2CN_2 + e^- \rightarrow Ph_2CN_2{}^{\cdot-} \qquad (1)$$

$$Ph_2CN_2{}^{\cdot-} \xrightarrow{H^+} Ph_2C{=}N\dot{N}H \xrightarrow{e^-,\ H^+} Ph_2C{=}NNH_2 \qquad (2)$$

$$Ph_2CN_2{}^{\cdot-} \xrightarrow{H^+} Ph_2CHN{=}\dot{N}: \xrightarrow{e^-,\ H^+} Ph_2CH_2 + N_2 \qquad (3)$$

$$Ph_2CN_2{}^{\cdot-} \xrightarrow{-N_2} Ph_2C^{\cdot-} \xrightarrow{e^-,\ 2H^+} Ph_2CH_2 \qquad (4)$$

Cyclic voltammetric studies of the reduction of Ph_2CN_2 at 0 °C show Ph_2CH^- to be the only oxidizable intermediate at scan rates in excess of 10 V s^{-1}. As the scan rate is decreased, the following sequence of kinetically linked intermediates is observed: $Ph_2CH^- \rightarrow Ph_2CH\bar{N}{-}N{=}CPh_2 \rightarrow Ph_2C{=}N{-}N{=}CPh_2{}^{2-}$. 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.[4] 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 $(Fl{=}N{-})_2$ (run 6). Subsequent control experiments demonstrated that $Fl{=}NNH^-$ is only slowly protonated by DEM and that it reacts rapidly with FlN_2 to form the azine.[4] Proton donors which protonate $Fl{=}NNH^-$ 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-α 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 $Ph_2C^{\cdot-}$.[5]

We thank the National Science Foundation for support of this research.

(*Received, 27th February* 1980; *Com.* 221.)

[1] J. M. Bakke, D. Bethell, P. J. Galsworthy, K. L. Handoo, and D. Jackson, *J. Chem. Soc., Chem. Commun.*, 1979, 890.
[2] R. N. McDonald, R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1977, **99**, 1268.
[3] R. N. McDonald, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1978, **100**, 995.
[4] R. N. McDonald, F. M. Triebe, and M. D. Hawley, unpublished results.
[5] R. N. McDonald, A. K. Chowdhury, and D. W. Setser, *J. Am. Chem. Soc.*, in the press; results of the gas-phase chemistry of cyclopentadienylidene 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.