Tetrahedron Letters,Vol.30,No.37,pp 4961-4964,1989
Printed in Great Britain

0040-4039/89 \$3.00 + .00
Pergamon Press plc

UNUSUAL REACTIONS RESULTING FROM THE ADDITION ON OLEFINS OF TRIFLUOROMETHYL RADICALS OBTAINED FROM DISSOCIATIVE ELECTRON TRANSFER BETWEEN ELECTROCHEMICALLY GENERATED AROMATIC ANION RADICALS AND TRIFLUOROMETHYL BROMIDE

Claude P. ANDRIEUX, Laurence GELIS and Jean-Michel SAVEANT

Laboratoire d'Electrochimie Moléculaire de l'Université Paris 7, Associé au CNRS ,
2, place Jussieu, 75251 Paris Cedex 05, France

Summary: *Dissociative electron transfer between the anion radical of terephthalonitrile and CF_3Br in the presence of olefinic compounds results in the formation of an addition radical which eventually dimerizes into 1,1,1,6,6,6-hexafluoro-3,4-diphenyl hexane, in the case of styrene. The same reaction carried out with the same anion radical and butyl vinyl ether yields 4-(1-trifluoromethyl-2-n-butyloxyethyl)benzonitrile.*

Dissociative electron transfer between the anion radical of terephthalonitrile and CF_3Br in the presence of styrene results in the formation of an addition radical which eventually dimerizes into 1,1,1,6,6,6-hexafluoro-3,4- diphenylhexane whereas, in the presence of butylvinyl ether, 4-(1-trifluoromethyl-2-butyloxyethyl)benzonitrile is obtained, implying that the addition radical couples with terephthalonitrile with elimination of one cyanide ion. These reactions are unusual with reference to the results of past investigations concerning the addition on olefins of perfluoroalkyl radicals deriving from the corresponding iodides and bromides [1-3]. Two main types of reaction have been described in this connection. One consists in the 1,2-addition of perfluoroalkyl iodides on carbon-carbon double bonds yielding the corresponding alkyl iodides [2], the reaction being induced thermally or photochemically [2a-c], electrochemically [2d], through reduction by soft nucleophiles [2e], by metals [2f], or by means of transition metal catalysts [2g]. The other is an hydroperfluoroalkylation of olefinic double bonds [3] starting from perfluoroalkyl iodides or bromides in the presence $CpTiCl_2$ [3a] or from perfluoroalkyliodides in the presence of copper bronzes [3b].

Terephthalonitrile (TPN) is reversibly reduced into its anion radical in DMF (figure 1). Upon addition of CF_3Br, the corresponding cyclic voltammetric wave loses its reversibility and increases catalytically featuring the dissociative electron transfer from terephthalonitrile anion radical to CF_3Br yielding the $CF_3^{\cdot}$ radical :

$$\mathrm{TPN} + e^- \rightleftharpoons \mathrm{TPN}^{\cdot -}$$

$$\mathrm{TPN}^{\cdot -} + CF_3Br \rightarrow \mathrm{TPN} + CF_3^{\cdot} + Br^-$$

which then abstracts an H-atom from the solvent [4]. Addition of styrene to the solution does not produce any significant change of the voltammogram, indicating either a lack of reaction or the occurence of a reaction that would not modify the overall electron stoichiometry. The latter was confirmed by preparative-scale electrolysis in the same solvent on a carbon electrode at the reduction potential of terephthalonitrile (– 1.6 V vs SCE) . 1,1,1,6,6,6-hexafluoro - 3,4 - diphenylhexane was obtained as revealed by ^{19}F NMR of the raw solution (ref. $CFCl_3$: $\delta = -64$ ppm t , $J_{CF_3\text{-}CH_2} = 10.3$ Hz) and by mass spec., ^{13}C, ^{1}H NMR of the extracted product (MS, m/e : 173) (CF_3CH_2CHPh), 109 (CF_3CH_2CHCH), 104 (CH_2CHPh).^{13}C NMR (ref. : TMS) : δ (ppm) : 125.7 - 132.3, 141.0-147.7 (arom.C), 110.2-113.3, 118.2-123.1 (CF_3), 37.5-39.2 (CH_2),30.8-35.8-44.6 (CH). ^{1}H NMR (ref. : TMS) : δ (ppm): 7.3 m (arom C), 3.0 double q ($CH\text{-}CH_2\text{-}CF_3$). Coupled CPV-MS revealed the presence of 20% of the meso isomer and 80% of the RR-SS isomer.

Number of electrons per molecule of terephthalonitrile	[CF_3Br] (M)	[Styrene] (M)	Faradaic yield in 1,1,1,6,6,6 - hexafluoro 3,4 diphenylhexane (%)
2	0.34	1.0	27
6	0.04	1.0	38
8	0.04	0.4	40

Table 1 : Faradaic yields in the mediated reduction of CF_3Br in presence of styrene (chemical yields toward CF_3Br or styrene are larger or at worst equal to the faradaic yield).

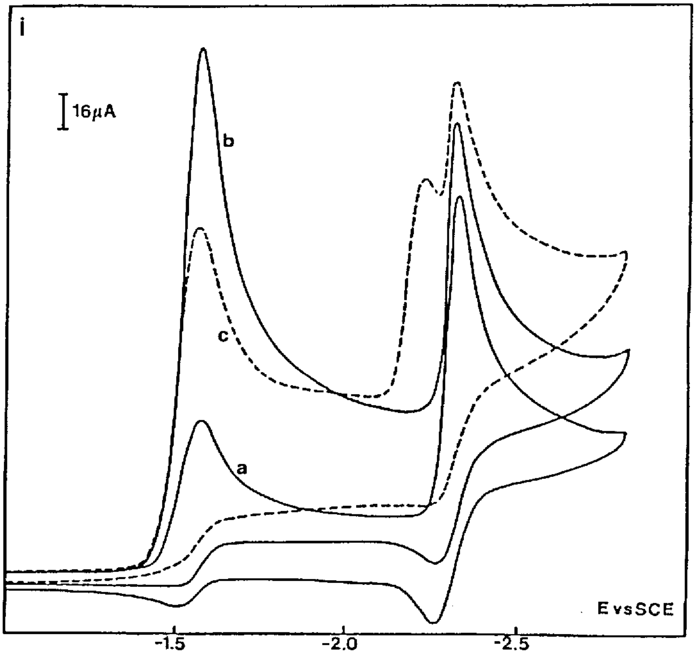
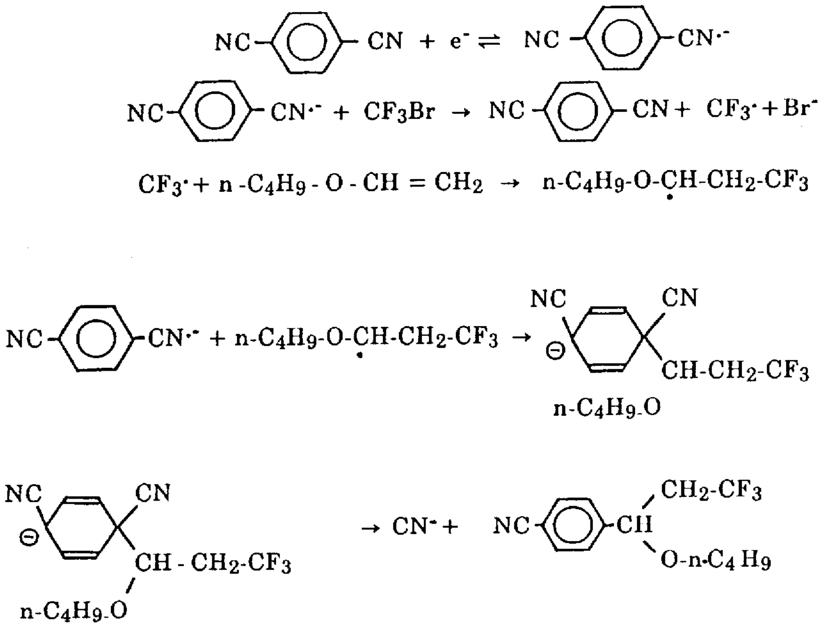


Figure 1. Cyclic voltammetry of terephthalonitrile (2mM) in DMF + 0.1 M NBu_4BF_4 at 20°C on a glassy carbon electrode at $0.2 Vs^{-1}$, alone (a), in the presence of 4.0 mM CF_3Br (b) and, in addition, of 20 mM butylvinyl ether (c).

Dimerization of alkyl radicals resulting from the addition of $CF_3^{\cdot}$ on olefins has previously been observed upon anodic generation of $CF_3^{\cdot}$ from trifluoroacetic acid or its derivatives[6]. It is remarkable that in the present case the same reaction can take place rather than the reduction of the addition benzyl radical using CF_3Br as a substrate under reducing conditions. This is made possible by the use of a mediator, terephthalonitrile anion radical, which allows the reduction of CF_3Br to be carried out at a much less negative potential than that of its direct reduction at an inert electrode [4], thus rendering the reduction of $Ph\dot{C}HCH_2CF_3$ slower than its dimerization.

A quite different reaction was observed when n-butylvinyl ether was used instead of styrene. In cyclic voltammetry (fig.1) addition of n-butylvinyl ether decreases the catalytic current down to a two-electron per terephthalonitrile molecule stoichiometry, the wave remaining irreversible. Concomitantly, a second two-electron irreversible wave appears in front of the second wave of terephthalonitrile. Electrolysis at -1.6 V vs SCE on a carbon electrode produced $CF_3CH_2CH(On\text{-}C_4H_9)C_6H_5CN$ in 95% yield (toward terephthalonitrile) as identified by ^{19}F NMR (ref. $CFCl_3$: $\delta = -64$ ppm t , $J_{CF_3\text{-}CH_2} = 10.3$ Hz), mass spec. (EI : 272 (M + 1), 198 ($CF_3CH_2CHC_6H_4CN$), 188 ($n\text{-}C_4H_9OCHC_6H_4CN$). ^{13}C NMR (TMS) δ (ppm) : 146.3 (arom.C-CN), 127.7 - 132.6 (other arom.C), 118.5 (CF_3), 112.3 (CN), 69.4 (CHO), 65 (CH_2O), 32 (CH_2CF_3) 19.8 - 19.5 ($(CH_2)_2$), 13.9 (CH_3). ^1H NMR (ref. TMS) δ (ppm) : 1.0 t (CH_3), 1.4 m (CH_2CH_2), 3.3 t (CH_2O), 3.4 - 3.m (CH_2CF_3), 4.6 - 4.7 m ($OCHCH_2$), 7.3 - 7.7 (phenyl)). The expulsion of one CN^- in this compound is quite similar to that previously observed to occur at the second one electron irreversible wave of terephthalonitrile where the dianion adds a proton and loses a cyanide ion [5]. This suggests the following mechanism :



It was checked that the second two-electron irreversible wave appearing upon addition of butylvinyl ether was the same as the wave obtained with an authentic sample of the electrolysis product The fact that a two-electron irreversible wave is obtained is presumably a result of the reductive cleavage of the benzylic ether bond[7].

Investigation of the reaction with other olefins and other aromatic anion radical is currently under way.

ACKNOWLEGMENT

Partial financial support from the ATOCHEM Company is gratefully acknowledged.

REFERENCES

1. (a) : Sheppard, W. A.; Sharts, C.M. "Organic Fluorine Chemistry", *Benjamin, New York,* 1969. (b) : Banks, R.E. "Fluorocarbons and Their Derivatives", *MacDonald, London,* 1970, p. 85. (c) : Chambers, R. D. "Fluorine in Organic Chemistry", *Wiley Interscience, New York,* 1973.

2 (a) : Tordeux, M.; Wakselman, C.; *Tetrahedron* 1980, *37*, 315. (b) : Brace, N.O. *J. Fluorine Chem.* 1982, *20*, 313. (c) : Baum, K.; Bedford, C.D.; Hunadi, R.J. *J. Org. Chem.* 1982, *47*, 2251. (d) : Calas, P.; Moreau, P.; Commeyras, A. *J. Chem. Soc. Chem. Comm.* 1982, 433. (e): Feiring, A. E. *J. Org. Chem.* 1985, *50*, 3269. (f) : Kuroboshi, M; Ishihara, T. *J. Fluorine Chem.* 1988, *39*, 299. (g) : Chen, Q. Y.; Yang, Z. Y.; Zhao, C . X.; Qiu, Z. M. *J. Chem. Soc. Perkin. Trans. 1* 1988, 563.

3. (a): Kitazume, T; Ischikawa, N. *J. Am. Chem. Soc.* 1985, *107*, 5186. (b) : Coe, P. L.; Milner, N. E. *J. Organometal. Chem* . 1972, *39*, 395.

4. Andrieux, C.P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. unpublished results.

5 (a) : Gennaro, A.; Romanin, A.M.; Severin, M.G.; Vianello, E. *J. Electroanal. Chem.* 1984, *169*, 279. (b) : *ibid* 1985, *185*, 353. (c) : Sertel, M., Yildiz; A.; Gambert, R.; Baumgärtel, H. *Electrochim. Acta* 1986, *31*, 1287 (d) : Gennaro, A.; Maye, A.; Maran, F.; Vianello, E. *Electrochim. Acta* 1988, *33*, 167. (e) : Yildiz, A.; Sertel, M.; Rambert, R.; Baumgärtel, H. *Electrochim. Acta* 1988, *33*, 169.

6. (a): Brookes, C.J.; Coe, P. L.; Owen, D. M.; Pedler, A.E.; Tatlow, J.C. *J. Chem. Soc. Chem. Comm.* 1974, 323. (b) : Renaud, R. N.; Champagne, J. *Can. J. Chem.* 1975, *53*, 529. (c) : Renaud, R.N.; Champagne, J. *Can. J. Chem.* 1979, *57*, 2617. (d) : Muller, N. *J. Org. Chem.* 1983, *48*, 1370. (e) : *ibid.* 1984, *49*, 2827. (f) : *ibid.* 4559. (g) : *ibid.* 1986, *51*, 263.

7. (a) : Garwood, R.F.; Naser-ud-din; Weedon, C.L. *J. Chem.Soc. Chem. Comm.* 1968, 923. (b) : Coleman, J.P.; Gilde, H.G.; Utley, J.P.H.; Weedon, C.L. *J. Chem. Soc. Chem.Comm.*, 1970, 738. (c) : Coleman, J.P.; Naser-ud-din; Gilde, H.D.; Utley, J.H.P.; Weedon, C.L.; Eberson, L. *J. Chem. Soc. Perkin. Trans. II.* 1973, 1903.

(Received in France 20 June 1989)