Tetrahedron Letters No. 25, pp 2089 - 2090, 1975. Pergamon Press. Printed in Great Britain.

RADICAL PATHS IN THE DECAY OF 2- AND 3-HALOTROPONE RADICAL ANIONS

by Massimo Martinelli,[iii] Lamberto Nucci,[i] Lucio Pardi,[ii] Francesco Pietra,[i] and Sergio Santucci[ii, iii]

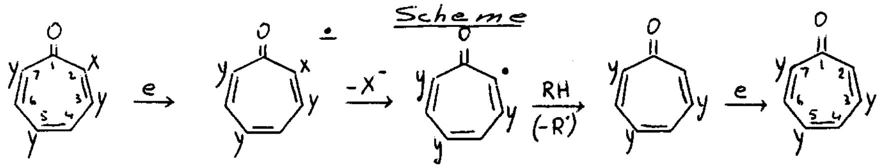
(Department of Chemistry,[i] Istituto di Fisica,[ii] Università di Pisa, and Gruppo Nazionale di Struttura della Materia del C.N.R.,[iii] Pisa)

(Received in UK 21 April 1975; accepted for publication 8 May 1975)

Recently there has been considerable electrochemical,[1] e.s.r. spectroscopic,[1] and synthetic interest[2] in electron transfers to organic halides. In this connection we report that 2- and 3-halotropone radical anions are generally unstable, giving tropone via a radical path which is unprecedented in the area of pseudo-aromatic compounds and has potential synthetic value.

Thus, cyclic voltammetry of 2-iodo- (1a) or 2-bromotropone (2a) in purified dimethylformamide (DMF) plus 0.1 M tetraethylammonium perchlorate showed cathodic peaks at, respectively, -1.240 and -1.210 V,[§] on either mercury or platinum, which could not be reversed at any sweep rate,[†] attributable to 2-iodo- (5a) and 2-bromotropone radical anions (6a), followed, in either case, by a cathodic peak at -1.400 V,[§] attributable to tropone radical anion (11a).

Scheme



1 X=I; 2 X=Br
3 X=Cl; 4 X=F

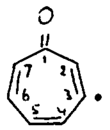
5 X=I; 6 X=Br
7 X=Cl; 8 X=F

9

10

11

a (Y = H) ; b (Y = D)



12

This was confirmed by parallel electrolytic reductions on a platinum grid directly in the cavity of an e.s.r. spectrometer, whereby the spectrum of 11a[3] was obtained. Also, starting from 3,5,7-trideuteriated halotropones 1b or 2b, an e.s.r. spectrum was obtained which is attributable to 3,5,7-trideuteriotropone radical anion (11b).[x]

Microcoulometry revealed that tropone is formed in an overall monoelectronic process, which is best explained by the radical mechanism at the scheme, where RH is a general hydrogen donor.

The behaviour of 3-chlorotropone is strictly similar to that above, the mechanism at the scheme requiring 12 in the place of 9.

In contrast, 2-chlorotropone (3a) gave a cathodic peak at -1.350 V,[§] attributable to 2-chlorotropone radical anion (7a) which proved to be less unstable than either 5a or 6a, giving 10a only as a minor by-product, the main decaying process being under investigation. E.s.r. spectroscopy so far revealed only the presence of 11a, besides unidentified signals. Parallel observations were made with 3b.

Finally, 2-fluorotropone (4a) gave a cathodic peak at -1.440 V,[§] attributable to 2-fluorotropone radical anion (8a) which proved to be the most stable of all radicals above, its e.s.r. spectrum being easy to record,[✣] no trace of tropone being detectable.

Whilst it is clear that the driving force for the radical processes at the scheme is contributed by the weakeness of the carbon-heavy halogen bonds, the fact that 12 is easily formed from 3-chlorotropone radical anion whereas 7a is reluctant to give 9a do not conform to recent theories relating the position of highest reactivity for aromatic compounds to that of highest spin density.[4] In fact, with cycloheptatrienone radical anions the spin density is generally maximal at C_2 and minimal at C_3.[5]

We currently pursue both goals of stabilizing 9 and 12 in a solid matrix for spectroscopic purposes and trapping 12 with nucleophiles as a general approach to so far unaccessible 3-substituted tropones.

NOTES AND REFERENCES

[§] With respect to the s.c.e.. [†] Instrument limits : 400 Vs^{-1}. [✗] The spectrum consists of 26 lines from which computer analysis gave hfsc 8.6, 5.0, 0.77, and 1.3 G for, respectively, H_2, H_4, D_5, and D_7. [✣] The spectrum consists of four blocks of three lines each in the relative intensity ratio 1:2:1, giving hfsc 20.0, 5.0, 5.0, and 8.6 G for F, H_4, H_5, and H_7, respectively. This is supported by the e.s.r. spectrum of 8b. Standard INDO calculations, which were found to reproduce nicely hfsc values for 3-methoxytropone radical anion,[5] could not be carried out for 8a because of a poor choice of the initial density matrix by the Hückel method. This was overcome by the choice, as the initial density matrix, of that obtained by the standard INDO method for closed shell 2-fluorotropone, suitably modified for addition of one electron, to give fully planar 8a with regular heptagon geometry, whereby we got 20.0, 2.82, 5.48, 3.41, 1.05, and 8.11 G for F. H_3, H_4, H_5, H_6, and H_7, respectively

1) See Annual Rept. Chem. Soc., 70, 289 (1973) for a summary.
2) See, inter alia, J.F. Bunnett, Accounts Chem. Res. 5, 139 (1972); F. Pietra and al. , Chem. Comm., 1232 (1971); J. A. Zoltewicz and T.M.Oestrich, J.Amer. Chem.Soc. 95 6863 (1973).
3) Y. Ikegami, H. Watanabe, and S. Seto, Bull.Chem.Soc.Japan, 45 1976 (1972).
4) K. Alwair and J. Grimshaw, J.C.S.PerkinII, 1150 and 1811 (1973).
5) C. Festa, A.M. Moresco, L. Nucci, L. Pardi, F. Pietra, and S. Santucci, submitted for publication.

ACKNOWLEDGMENTS

Financial support by the C.N.R., Roma, for the work carried out at the Department of Chemistry is acknowledged