Journal of Fluorine Chemistry, 12 (1978) 337-340

Received: May 10, 1978

PRELIMINARY NOTE

Photochemical Transformations of Perfluoro-tri- and -tetra-methylfurans

R.D. CHAMBERS*, A.A. LINDLEY

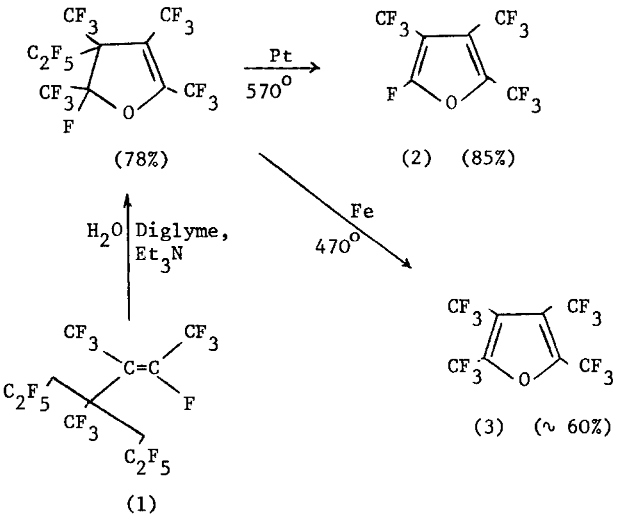
Department of Chemistry, University Science Laboratories, South Road,
Durham City, DH1 3LE, U.K.

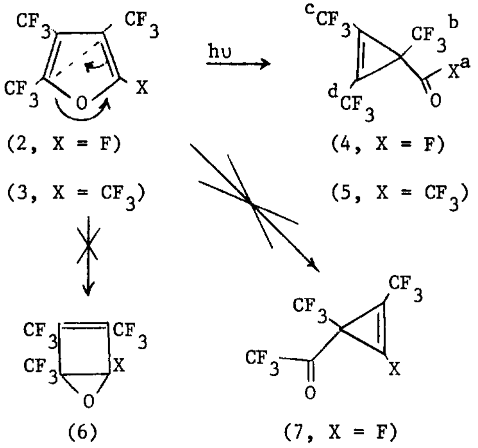
and H.C. FIELDING

I.C.I. Ltd., Mond Division, R. & D. Department, P.O. Box No. 8, The Heath,
Runcorn, Cheshire, U.K.

The recent publications by Kobayashi[1] and Lemal,[2] together with their respective co-workers, on the synthesis of perfluorotetramethylfuran, prompts us to report some of our findings in this area. These reported syntheses of perfluorotetramethylfuran (3) essentially start with hexafluoro-2-butyne while we have recently synthesised both perfluorotetramethylfuran (3) and perfluoro-2,3,4-trimethylfuran (2) from tetrafluoroethylene oligomers obtained by fluoride-ion induced processes. One such route, from the pentamer of tetrafluoroethylene (1), is shown overleaf.[3]

As indicated by other workers,[1,2] the photochemistry of fluorinated furans is of special interest because of the possibility of obtaining valence isomers, e.g. a Dewar furan, but these workers were unable to obtain photochemical products from (3). We have now observed low (ca. 20%) conversions of both (2) and (3), under transfer conditions[4] past a high pressure Hg lamp, to cyclopropenylcarbonyl derivatives (4) and (5). The spectral data for (5) are identical with the reported data,[2] while compound (4) is easily characterised by comparison of the spectral data with that obtained for (5); i.r. (vapour) 1935 ($\upsilon_{C=C}$), 1900, 1860 ($\upsilon_{C=O}$), 1350 - 1170 (υ_{C-F}), 1015, 950, 800, 700, 660 cm.$^{-1}$; ^{19}F δ^5 -29.7 (Int. 1, F-a, $J_{a,b}$ = 10 Hz) +63.6 (Int. 6, F-c,d), 70.4 p.p.m. (Int. 3, F-b).

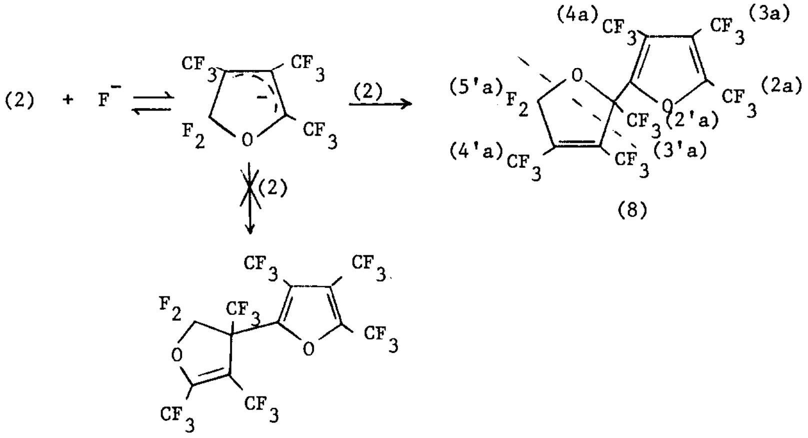




No Dewar furan derivatives (6) were detected, in contrast to the observed photochemical transformation of perfluorotetramethylthiophene to a Dewar form.[6,7] The different behaviour of (2) and (3) is probably a consequence of the greater strength of the carbon-oxygen than the carbon-sulphur double bond and the furan-cyclopropenylketone rearrangements observed for (2) and (3) are examples of a photochemical transformation that is now well established for non-fluorinated furan derivatives.[8]

It is interesting that ring opening of the furan derivative (2) occurred specifically, giving the acid fluoride (4), rather than the ketone (7). This special selectivity could be a result of either the destabilising influence of a fluorine atom directly attached to a carbon-carbon double bond,[9] as in (7), a stabilising influence of trifluoromethyl groups on small rings,[2,10] as in (4), or a combination of both factors.

Work is proceeding on other chemistry of the furan derivatives (2) and (3), and of the novel derivative (8), which is formed in high yield by reactions of (2) with caesium fluoride in tetraglyme at room temperature. Of the two possible dimers (8) and (9), only (8) was observed and the structure was established mainly through a metastable peak in the mass-spectrum, which indicates loss of a C_5F_8 fragment. This is clearly possible from (8) but not from (9).

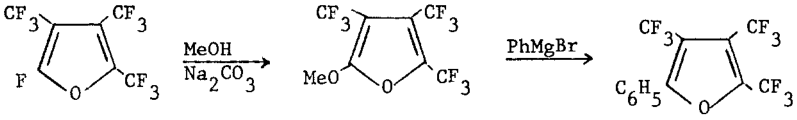


(8)

(9)

The i.r. spectrum of (9) showed bands in the region for ($\nu_{C=C}$) at 1580 (M), 1630(M), 1715(W), and 1755(W) $cm.^{-1}$; ^{19}F δ^5, 57.3 (quartet, 4a-F), 59.3 (septet, 3a-F), 60.8 (multiplet, 3'a-F), 63.3 (multiplet, 4'a-F), 64.5 (quartet, 2a-F), 61.5, 66.3 (AB/J = 150 Hz, 5'-F), 74.3 (multiplet, 2'a-F) p.p.m.

Other fluorinated furan derivatives may be obtained by nucleophilic attack on perfluoro-2,3,4-trimethylfuran (2) e.g. (9) and (10) may be obtained by reaction of (2) with methanol and phenylmagnesium bromide respectively and the photochemistry of (9) and (10) is currently under investigation.



(2) (9) (10)

ACKNOWLEDGEMENT

We thank I.C.I. Ltd. for financial support.

REFERENCES

1 Y. Kobayashi, Y. Hanzawa, Y. Nakanishi, and T. Kashiwagi, Tetrahedron Lett., (1978) 1019.

2 C.J. Boriack, E.D. Laganis, and D.M. Lemal, Tetrahedron Lett., (1978) 1015.

3 R.D. Chambers, A.A. Lindley, H.C. Fielding, J.S. Moilliet, and G. Whittaker, Chem. Comms., submitted for publication.

4 R.D. Chambers, J.R. Maslakiewicz, and K.C. Srivastava, J. Chem. Soc. Perkin I, (1975) 1130.

5 Using $CFCl_3$ as external reference; positive shifts are upfield from the reference.

6 H.A. Wiebe, S. Braslavsky, and J. Heicklen, Can. J. Chem., 50 (1972) 2721.

7 Y. Kobayashi, I. Kumadaki, A. Ohsewa, and Y. Sekine, Tetrahedron Lett., (1974) 2841.

8 E.E. van Tamelen and T.H. Whitesides, J. Amer. Chem. Soc., 93 (1971) 6129.

9 R.D. Chambers, 'Fluorine in Organic Chemistry', Wiley-Interscience, New York (1973) p.144.

10 D.M. Lemal and L.H. Dunlap, J. Amer. Chem. Soc., 94 (1972) 6562.