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PRELIMINARY NOTE

Some Reactions of Potassium N-Trifluoromethylsulphamate N-Oxyl

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SUMMARY

Aqueous potassium N-trifluoromethylsulphamate N-oxyl combines with tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, and acrylonitrile to yield 2:1 adducts, isolable as the bis-tetraphenylarsonium salts, $Ph_4As^+ \ CF_3N(SO_3^-)\cdot OCX_2CYZON(SO_3^-)CF_3 \ {}^+AsPh_4$ (X=Y=Z=F; X=Y=F, Z=H; X=Y=F, Z=Cl; X=Y=H, Z=CN), and abstracts hydrogen from hydroxylamine to yield nitrous oxide.

While publications dealing with Fremy's radical [$\cdot ON(SO_3^-K^+)_2$ (I)] [1] and the so-called magic radical [$(CF_3)_2NO\cdot$ (II)] [2] abound, only a single paper based on the structural hydrid of these two oxyls, *viz*. potassium N-trifluoromethylsulphamate N-oxyl, $CF_3N(\dot{O})SO_3^-K^+$ (III), exists [3]; this contains details

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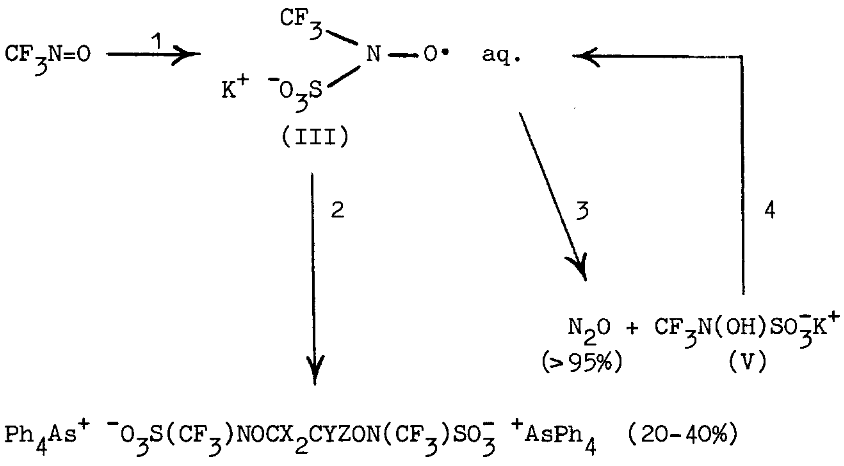

SCHEME

Reagents: 1 $KHSO_3$ aq. + PbO_2 [3]; 2 CX_2=CYZ (X=Y=Z=F; X=Y=F, Z=Cl; X=Y=F, Z=H; X=Y=H, Z=CN) followed by $Ph_4As^+Cl^-$ aq.; 3 NH_2OH, HCl; 4 PbO_2.

of the preparation of aqueous (purple) solutions of (III) (and of its sodium analogue) from trifluoronitrosomethane, of its e.s.r. parameters, and of its conversion into the water-insoluble tetraphenylarsonium derivative $CF_3N(\dot{O})SO_3^-Ph_4As^+$ (IV). Further information about (III) (see the Scheme) has now become available through work aimed at the development of new routes to fluorocarbon systems carrying sulphonate and related groups.

Deep purple solutions of potassium N-trifluoromethylsulphamate N-oxyl (III) were prepared by treating an excess of trifluoronitrosomethane with aqueous potassium bisulphite in the presence of lead dioxide at room temperature. The yield of (III) [estimated by adding $Ph_4As^+Cl^-$ to solutions to cause precipitation of $CF_3N(\dot{O})SO_3^-$ ions as (IV)] was never greater than 12% (based on HSO_3^-) owing to competition between PbO_2-oxidation of the radical precursor $CF_3N(OH)SO_3^-K^+$ formed first and hydrolysis of that species to bisulphate ion and the hydroxylamine CF_3NHOH (V), and thence inorganic entities {NH_2OH which is capable of destroying (III) (see the Scheme), CO_2, and HF}. N-Trifluoromethylhydroxylamine (V) was isolated as an etherate (a 'trick' used previously during work on reduction of CF_3NO with HI [4]) following treatment of trifluoronitrosomethane with aqueous potassium bisulphite alone in the presence of diethyl ether.

Like potassium nitrosodisulphonate (I), which decomposes in buffered acidic solutions according to the equation $4\ {\cdot}ON(SO_3^-)_2 + 3\ H_2O = 2\ HON(SO_3^-)_2 + N_2O + 4\ HSO_4^-$ [5], potassium N-trifluoromethylsulphamate N-oxyl (III) decays in water, solutions prepared as described previously [3] becoming colourless and evolving trifluoronitrosomethane during the space of 2-3 h. Immediate addition of lead dioxide to a just colourless solution caused reappearance of the characteristic purple colour associated with the oxyl, which prompts one to speculate that the 'bleaching' process involves the reaction $2\ CF_3N(\dot{O})SO_3^- + CF_3NHOH \longrightarrow 2\ CF_3N(OH)SO_3^- + CF_3NO$ {cf. [6] 2 t-BuN($\dot{O}$)COPh + t-BuNHOH $\longrightarrow$ 2 t-BuN(OH)COPh + t-BuNO}. Addition of potassium acetate as a buffer to freshly procured solution considerably delays complete loss of colour (up to 24 h),* so reactions 2 and 3 in the Scheme were carried out with this agent present; consumption of the oxyl (III) was complete within 3 h ($CF_2{=}CF_2$, 50 min.; $CF_2{=}CFCl$, 40 min.; $CF_2{=}CHF$, 3 h; $CH_2{=}CHCN$, 2 h 45 min.;

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*Frozen solutions [yellow in colour, presumably owing to dimerization of (III)] have been stored for up to 17 days at -196 °C without loss of the oxyl.

NH_2OH, instantaneous), and products were identified by standard procedures. The ability of the oxyl (III) to attack tetrafluoroethylene** is seemingly [7] not shared by Fremy's radical (I), so this trait stems from the fluorocarbon side of the family, (II). Like Fremy's radical, (III) rapidly oxidises hydroxylamine to nitrous oxide at ambient temperature; provided an excess of the substrate is avoided, the N-trifluoromethylhydroxylamine N-sulphonate (V) formed concomitantly can be detected by addition of lead dioxide to the spent reaction medium.

1 For a review, see H. Zimmer, D.C. Lankin, and S.W. Horgan, Chem. Rev., 71 (1971) 229.

2 For reviews, see R.E. Banks, 'Fluorocarbon and Related Chemistry' (C.S. SPR Series), 1 (1971) 109; 2 (1974) 223; 3 (1976) 235.

3 R.E. Banks, D.J. Edge, J. Freear, and R.N. Haszeldine, J. Chem. Soc. Perkin Trans. I, (1974) 721.

4 A. Ya. Yakubovich, V.A. Ginsburg, S.P. Makarov, V.A. Shpanskii, L.L. Martynova, B.V. Kir'yan, and A.L. Lemke, Dokl. Adad. Nauk S.S.S.R., 140 (1961) 1352.

5 J.H. Murib and D.M. Ritter, J. Amer. Chem. Soc., 74 (1952) 3394.

6 S.A. Hussain, T.C. Jenkins, and M.J. Perkins, J. Chem. Soc. Perkin Trans. I, (1979) 2809.

7 M.J. Stevenson, personal communication.

8 H. Gehlen and G. Dase, Z. anorg. Chem., 275 (1954) 327.

**No information on addition reactions between Fremy's radical and alkenes could be found in the literature.