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PRELIMINARY NOTE

# Reaction of Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) with Monohalogenobenzenes

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SUMMARY

Reaction of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (I) with chlorobenzene or bromobenzene affords mainly the substitution products $(CF_3)_2NC_6H_4X$ (X=Cl or Br; para>ortho>meta). In contrast reaction with fluorobenzene gives mainly addition products, i.e. cyclohexenes, and the compound $4\text{-}(CF_3)_2NOC_6H_4N(CF_3)_2$, while reaction with iodobenzene yields the compounds $(CF_3)_2NH$ and $4\text{-}IC_6H_4I$ and tar.

Three multistage routes to NN-bistrifluoromethylaniline (II) and its derivatives have been reported [1-3] as well as a two-stage synthesis from benzaldehyde [4], i.e.

$$PhCHO \xrightarrow{(CF_3)_2NO^{\bullet}} \underset{(III)}{PhCO_2N(CF_3)_2} \longrightarrow \underset{(II)}{PhN(CF_3)_2}$$

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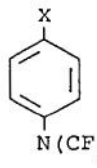
but a later investigation of the pyrolysis of compound (III) under a variety of conditions failed to obtain evidence for the formation of compound (II) [5].

We then reported a novel one-step synthesis of derivatives of (II) of type $(CF_3)_2NC_6H_4X$ (X=$Me_3C$, H, OH, OMe, $NO_2$ and Cl) in reasonable yield by reaction of the oxadiazapentane (I) with the appropriate arene PhX [6]. This method was then extended to the synthesis of $(CF_3)_2N$-substituted pyridines [7].

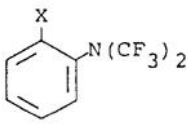
In the present work the reaction of the oxadiazapentane (I) with the monohalogenobenzenes PhX (X=F, Br and I) at room temperature has been investigated and the results obtained are given in the Table (Formulae below) together with those reported previously for the reaction involving chlorobenzene [6].

$(CF_3)_2NH$ (IV)

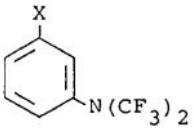
$(CF_3)_2NOH$ (V)



(VI) X=$ON(CF_3)_2$
(IX) X=Cl
(XII) X=Br

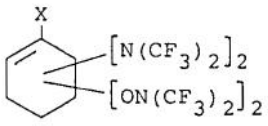


(VII) X=Cl
(X) X=Br



(VIII) X=Cl
(XI) X=Br

(XIII)



(XIV) X=F, Cl or Br

By comparison with the accepted mechanism for the addition of the oxadiazapentane (I) to alkenes [8] it has been suggested that reaction with arenes involved initial homolytic fission of a weak N-O bond in (I) followed by $(CF_3)_2N^{\cdot}$ radical attack on the arene to give intermediate radicals of type (XV) [6]. Further reaction of the radicals (XV) can then occur with (I), $(CF_3)_2N^{\cdot}$ or $(CF_3)_2NO^{\cdot}$ to afford the observed products.

TABLE

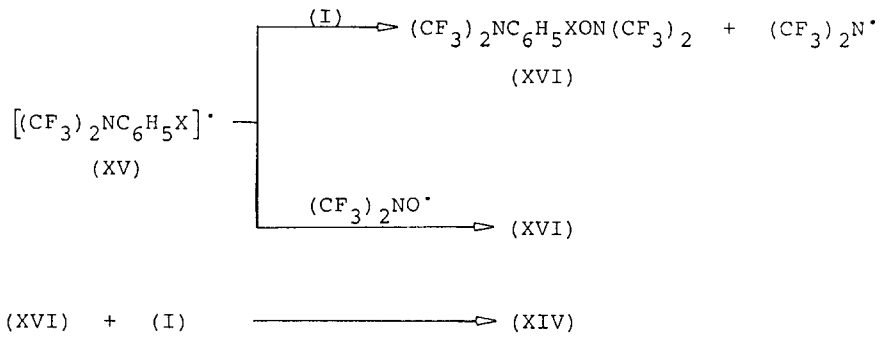
Reaction of the oxadiazapentane (I) with monohalogenobenzenes

| X in PhX | (g, mmole) | (I) (g, mmole) | Time (d) | PhX recovered (%) | Products* (% yield) |
|---|---|---|---|---|---|
| F | (1.51, 15.9) | (5.22, 16.3) | 4 | ca. 30 | (IV) (18), (V) (16), (VI) (20) |
| Cl | (1.04, 9.2) | (2.94, 9.3) | 16 | 42 | (IV) (15), (V) (35.5), (VI) (4.5), (VII) (9), (VIII) (6), (IX) (44.5), HCl (4) |
| Br | (2.25, 14.3) | (5.15, 16.1) | 18 | 17 | (IV) (20), (V) (14), (VI) (4), (X) (21), (XI) (11), (XII) (38), HBr (8) |
| I | (1.70, 8.3) | (3.30, 10.3) | 45 | 6 | (IV) (95), (V) (trace), (XIII) (93) |

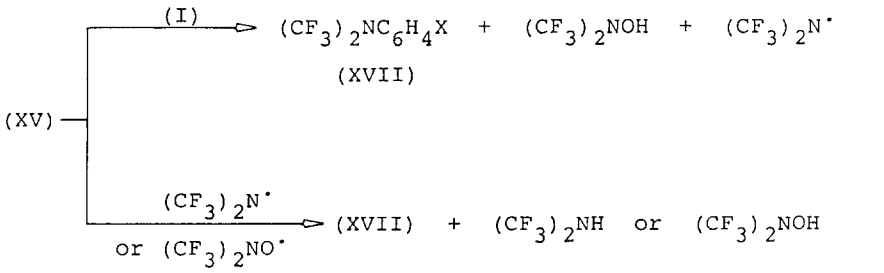
*The yields of products are based on PhX used except for compounds (IV) and (V) which are based on (I). The reactions of the arenes PhX (X=F, Cl and Br) also gave higher-boiling material (the major product with PhF), which consisted mainly of 2:1 adduct isomers of type (XIV) as shown by g.l.c.-mass spectrometry, while the iodobenzene reaction gave an intractable tar.

The results obtained from the halogenobenzene reactions (except PhI) can be explained by this radical mechanism, but a contribution, at least in part, from a one-electron transfer mechanism cannot be discounted. A detailed discussion of the mechanism covering the reaction of (I) with both the arenes and pyridines is deferred to a full paper.

If intermediate radicals of type (XV) are involved those formed by ortho-, meta- or para-attack on fluorobenzene undergo further reaction to give mainly addition compounds, i.e. where X=F

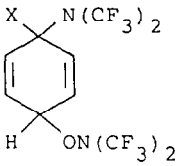



In contrast the radicals (XV) formed from the arenes PhCl and PhBr react further mainly by hydrogen abstraction, i.e. where X=Cl or Br

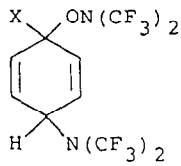


The substitution products (XVII) formed from chlorobenzene and bromobenzene (statistical ratios allowing for only one para position; o:m:p ca. 9:6:85 and ca. 20:10:70, respectively) indicate that the halogen has a strong para-directing influence and that ortho-attack is governed mainly by electronic not steric effects.

It is interesting to note that a much higher yield of compound (VI) was obtained from the fluorobenzene reaction than from the chlorobenzene or bromobenzene reactions. Compound (VI) is considered to arise by dehydrohalogenation of the 1:1 adducts (XVIII) or (XIX) formed via ipso- and para-attack, respectively.

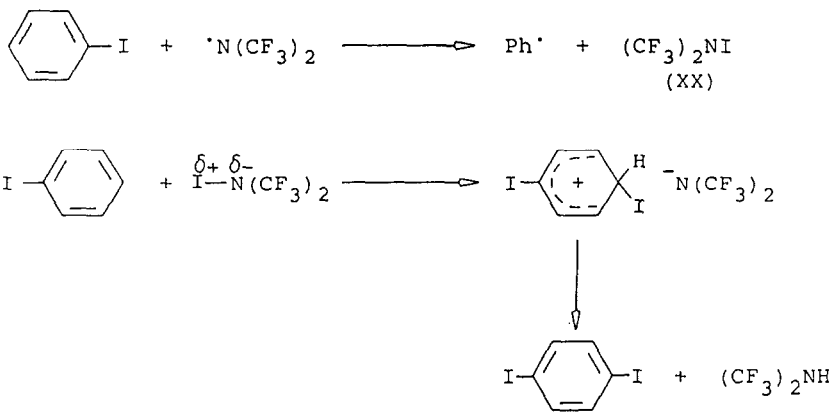


(XVIII)



(XIX)

The isolated products from the iodobenzene reaction can be explained by $(CF_3)_2N^{\bullet}$ radical attack occurring on the halogen atom rather than on the ring followed by electrophilic iodination of a second iodobenzene molecule by the resulting N-iodoamine (XX), i.e.



The structures of the products were established spectroscopically [i.r., n.m.r. ($^{1}H$ and $^{19}F$), and mass] and all possessed correct elemental compositions. Compounds (X), (XI), (XII) and (XIV) (X=F and Br) are new.

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