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PRELIMINARY NOTE

Novel One-step Synthesis of (Bistrifluoromethylamino)benzenes

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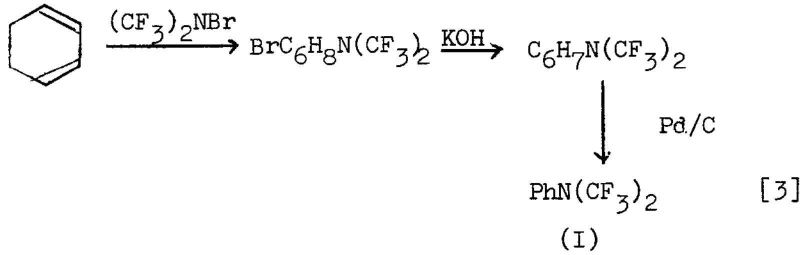
The following multi-stage routes (a-c) to NN-bistrifluoromethylaniline (I) and its derivatives have been reported.

(a)
$$\begin{tikzcd} PhNHMe \arrow[r, "i)CSCl_2", "ii)Cl_2"'] & 4\text{-}ClC_6H_4NMeCCl_3 \arrow[d, "i)SbF_3", "ii)Cl_2"'] \\ 4\text{-}ClC_6H_4N(CF_3)_2 & 4\text{-}ClC_6H_4N(CF_3)CCl_3 \arrow[l, "SbF_3/Sb_5"'] \end{tikzcd}$$ [1]

(b)
$$\begin{tikzcd} ArNH_2 \arrow[r, "CSCl_2"] & ArNCS \arrow[r, "HgF_2"] & ArN{=}CF_2 \arrow[r, "F^-/COF_2"] & ArN(CF_3)COF \arrow[dl, "SF_4/HF"] \\ & & ArN(CF_3)_2 & \end{tikzcd}$$ [2]

(c)

$$\begin{tikzcd} \arrow[r, "(CF_3)_2NBr"] & BrC_6H_8N(CF_3)_2 \arrow[r, "KOH"] & C_6H_7N(CF_3)_2 \arrow[d, "Pd/C"] \\ & & PhN(CF_3)_2 \end{tikzcd}$$ [3]

(I)

A two-step synthesis (d) has also been reported [4], but in our hands pyrolysis of the oxy-carbonyl compound under a variety of conditions including those published did not give the aniline I.

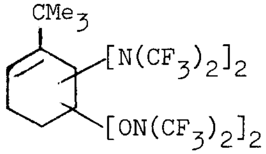
$$\text{(d)}\quad \mathrm{PhCHO} \xrightarrow{(CF_3)_2NO\cdot} \mathrm{PhCO_2N(CF_3)_2}\ [5] \xrightarrow{\Delta} \text{(I) (30\%)}$$

During an investigation of free-radical rearrangements initiated by $(CF_3)_2N\cdot$ radical abstraction of hydrogen [6] the reaction of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (II) with t-butylbenzene was studied. The expected rearrangement product III was not detected but the $(CF_3)_2N$ - substituted arenes IV and V were isolated together with 2:1 adducts VI.

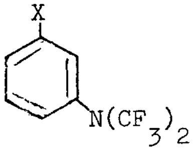
This observation prompted an investigation of the reaction of the oxadiazapentane (II) with benzene and various substituted benzenes and the results obtained are shown in the Table.

$PhCH_2CMe_2ON(CF_3)_2$

(III)



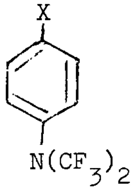
(VI)



(IV) X=CMe_3

(XV) X=NO_2

(XVIII) X=Cl



(V) X=CMe_3

(X) X=OMe

(XIII) X=OH

(XVI) X=$ON(CF_3)_2$

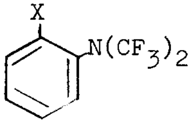
(XIX) X=Cl

$(CF_3)_2NH$

(VII)

$(CF_3)_2NOH$

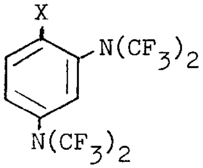
(VIII)



(IX) X=OMe

(XII) X=OH

(XVII) X=Cl



(XI) X=OMe

(XIV) X=OH

TABLE

Synthesis of (bistrifluoromethylamino)benzenes from arenes and $(CF_3)_2NON(CF_3)_2$ (II)

X in PhX	(g, mmole)	(II) (g, mmole)	Conditions (Temp °C, Time d)	Products* (% yield)
Me_3C	(0.86, 6.4)	(2.0, 6.3)	(20, 7)	(IV)(31.5), (V)(40),(VI)(17),(VII)(9), (VIII)(47)
H	(0.74, 9.5)	(3.43, 10.7)	(20, 21)	(I)(60), (VII)(9), (VIII)(48)
OMe	(1.28, 11.85)	(3.29, 10.3)	(20, 27)	(VII)(13), (VIII)(56), (IX)(30), (X)(55), (XI)(2)
OH	(1.46, 15.5)	(4.88, 15.3)	(20, 7)	(VII)(85), (VIII)(44), (XII)(4), (XIII)(6), (XIV)(1)
NO_2	(1.48, 12.0)	(3.37, 10.5)	(70-75, 7)	(VII)(65), (VIII)(15), (XV)(40)
Cl	(1.04, 9.2)	(2.94, 9.3)	(20, 16)	(VII)(15), (VIII)(35.5), (XVI)(4.5), (XVII)(9), (XVIII)(6), (XIX)(44.5), HCl(4)

* The reactions of the arenes PhX (X = H, OMe, and Cl) also gave higher-boiling material probably consisting mainly of 2:1 adducts analagous to (VI), while the nitrobenzene reaction gave higher-boiling material and an intractable tar and the phenol reaction gave an intractable tar.

The phenols (XII) and (XIII) have also been prepared by static pyrolysis _in vacuo_ of the amino-oxybenzene $PhON(CF_3)_2$ at _ca_. 110 °C [7] and flow pyrolysis _in vacuo_ of the aryl carbonate $PhOCO_2N(CF_3)_2$ at 660 °C [8]. By analogy with the accepted mechanism for the addition of the oxadiazapentane (II) to alkenes [9] the following free-radical pathway is proposed to explain the major products.

$$\underset{\text{(II)}}{(CF_3)_2NON(CF_3)_2} \longrightarrow (CF_3)_2N\cdot + (CF_3)_2NO\cdot$$

$$(CF_3)_2N\cdot + ArH \longrightarrow \underset{\text{(XX)}}{(CF_3)_2NArH\cdot}$$

$$\text{(XX)} + \text{(II)} \longrightarrow \begin{cases} (CF_3)_2NAr + (CF_3)_2NOH + (CF_3)_2N\cdot \\ \underset{\text{(XXI)}}{(CF_3)_2NArHON(CF_3)_2} + CF_3)_2N\cdot \end{cases}$$

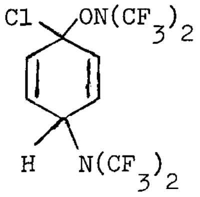
$$\text{(XX)} + (CF_3)_2N\cdot \longrightarrow (CF_3)_2NAr + (CF_3)_2NH$$

$$\text{(XX)} + (CF_3)_2NO\cdot \longrightarrow \begin{cases} (CF_3)_2NAr + (CF_3)_2NOH \\ \text{(XXI)} \end{cases}$$

$$\text{(XXI)} + \text{(II)} \longrightarrow [(CF_3)_2N]_2ArH[ON(CF_3)_2]_2$$

The orientation of attack on the aromatic rings is as expected for reaction with an electrophile in agreement with the $(CF_3)_2N\cdot$ radical being highly electrophilic [10]. The apparent strong _para_ - directing effect of the chlorine in chlorobenzene was unexpected since the $CF_3\cdot$ and $(CF_3)_2N\cdot$ radicals have been considered to be of comparable electrophilicity [10] and reaction of $CF_3\cdot$ radicals (generated from CF_3I + u.v.) with chlorobenzene gives $CF_3C_6H_4Cl$ (_o_:_m_:_p_ = _ca_. 50:25:25) [11].

Compound (XVI) is considered to be formed by elimination of hydrogen chloride (an observed product) from the 1:1 adduct (XXII).



(XXII)

The low yield of $(CF_3)_2N$ - substituted arenes from the phenol reaction is attributed to the preferential abstraction of hydrogen from the OH group by the $(CF_3)_2N\cdot$ radical.

The structures of the products were established spectroscopically [i.r., n.m.r. (^1H and ^{19}F), and mass] and all possessed correct elemental compositions.

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