Evidence for Nitrene Formation *via* Pyrolysis of an *NN*-Dihalogenoaniline: Thermal Conversion of *NN*-Dichloroperfluoro-*p*-toluidine into Perfluoro-(2-dichloromethyl-4-methylpyridine) and Perfluoro-(1-cyano-4-methylcyclopenta-1,3-diene)

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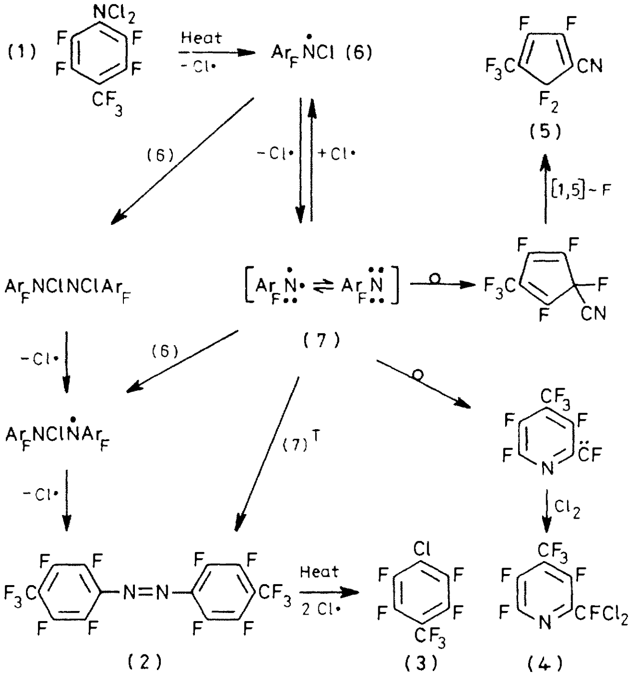
Summary Flow pyrolysis of *NN*-dichloroperfluoro-*p*-toluidine at 550 °C and *ca.* 1 mmHg yields, *inter alia*, perfluoro-4,4′-azotoluene, perfluoro-4-chlorotoluene, perfluoro-(2-dichloromethyl-4-methylpyridine) and perfluoro-(1-cyano-4-methylcyclopenta-1,3-diene); formation of the last two compounds suggests that perfluoro-*p*-tolylnitrene is implicated.

The potential[1] of *NN*-dihalogenoanilines as progenitors of arylnitrenes remains untapped, despite the passage of more than half a century since Goldschmidt[2] pointed out that azo-compound formation *via* thermal decomposition of *NN*-dichloroanilines can be ascribed to the generation of arylnitrogen 'radicals', which he formulated in the manner ArN< [Ar = C_6H_5, $O_2NC_6H_4$ (*o*, *m*, *p*), C_6Cl_5, *etc.*]. This situation is understandable when one considers the hazards associated with the tendency of *NN*-dichloroanilines to rearrange exothermically to ring-chlorinated anilines, a problem which Goldschmidt attempted to overcome by chlorinating (HOCl) anilines carrying electron-withdrawing nuclear substituents; this led to the isolation of *NN*-dichloropentachloroaniline,[2b] the only[3] *NN*-dichloroarylamine capable of manipulation in comfort until compounds of the fluorocarbon class became available.[4–6] Of these, *NN*-dichloroperfluorotoluidine (**1**)[5] was chosen to put Goldschmidt's hypothesis to the test, owing to its reluctance to rearrange 'spontaneously' to the corresponding *N*,4-dichlorocyclohexa-2,5-dienylideneamine.[4–6]

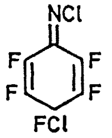


$Ar_F = p\text{-}CF_3C_6F_4$

SCHEME

Flow pyrolysis of (**1**) in silica apparatus at 550 °C and *ca.* 1 mmHg yields chlorine and a complex mixture of organic products from which it has proved possible to isolate perfluoro-4,4′-azotoluene (**2**; 5% yield), perfluoro-4-chlorotoluene (**3**; 30%), perfluoro-(2-dichloromethyl-4-methylpyridine) (**4**; *ca.* 15%), and a small amount of perfluoro-(1-cyano-4-methylcyclopenta-1,3-diene) (**5**). At lower temperatures, with a similar contact time, the yield of the azo-compound (**2**) increases [>26% at 200 °C based on *ca.* 50% decomposition of (**1**)] at the expense of the chloro-compound (**3**); 'flash' pyrolysis (*i.e.* rapid heating) of the dichloroamine (**1**) to 160 °C at 760 mmHg provides the azo-compound in at least 79% yield.[5]

From the nature of these products and from the observation that low-pressure flow chlorinolysis of perfluoro-4,4′-azotoluene at 550 °C provides the corresponding chloro-compound (**3**) in 92% yield, we conjecture that the steps shown in the Scheme are operative. The formation of the azo-compound in the first place can be ascribed to dimerization of the resonance-stabilized nitrogen-centred radical (**6**) or reactions of perfluoro-*p*-tolylnitrene (**7**); in the light of what is known about arylnitrenes of the hydrocarbon class,[7] much more convincing evidence for the generation of the latter transient intermediate is provided by the occurrence of *both* a benzene (**1**) → pyridine (**4**) isomerization and a ring-contraction leading to a cyanocyclopentadiene (**5**). All the transformations detected upon pyrolysis of (**1**) find analogies in the decomposition of the chloroimine



(**8**)

(**8**) at 550 °C, which lends credence to the postulate that the latter substrate suffers loss of the 4-chlorine initially.[8]

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[1] P. A. S. Smith in 'Nitrenes,' ed. W. Lwowski, Wiley-Interscience, New York, 1970, pp. 100, 103.

[2] (*a*) S. Goldschmidt, *Ber.*, 1913, **46**, 2728; 1920, **53**, 28; (*b*) S. Goldschmidt and L. Strohmenger, *ibid.*, 1922, **55**, 2450.

[3] We have been unable to substantiate the claim made by contemporaries of Goldschmidt (W. Eller and L. Klemm, *Ber.*, 1922, **55**, 217) that chlorination of *p*-aminophenol with sulphuryl chloride provides the isolable *NN*-dichloroamine $p\text{-}HOC_6Cl_4NCl_2$; in our hands (R. E. Banks and M. Mamaghani, unpublished results), the reaction yields the isomeric product $O{:}\overline{CCCl_2CCl_2C(:NH)CCl{:}C}Cl$.

[4] R. E. Banks and T. J. Noakes, *J. Chem. Soc., Perkin Trans.* 1, 1976, 143; R. E. Banks, M. G. Barlow, J. C. Hornby, and T. J. Noakes, *J. Fluorine Chem.*, 1979, **13**, 179; R. E. Banks, M. G. Barlow, J. C. Hornby, and M. Mamaghani, *J. Chem. Soc., Perkin Trans.* 1., 1980, 817.

[5] R. E. Banks, M. G. Barlow, T. J. Noakes, and M. M. Saleh, *J. Chem. Soc., Perkin Trans.* 1, 1977, 1746.

[6] Yu. G. Shermolovich, O. M. Polumbrik, L. N. Markovskii, E. P. Saenko, G. G. Furin, and G. G. Yakobson, *J. Org. Chem. U.S.S.R.* (*Engl. Transl.*), 1977, **13**, 2404.

[7] C. Wentrup, *Top. Curr. Chem.*, 1976, **62**, 173.

[8] B. A. Al-Saleh, R. E. Banks, M. G. Barlow, and J. C. Hornby, *J. Fluorine Chem.*, 1978, **12**, 341.