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Fluorination of Hexachlorobenzene with Antimony Pentafluoride

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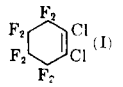
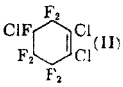
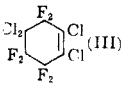
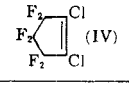
The reaction of hexachlorobenzene with antimonypentafluoride has been described in the literature,[1] but further work has shown some unreported facts. Care must be taken in heating the reaction mixture since at 160° there is a large evolution of heat which will cause loss of product unless cooling is used.

In the original procedure the only product described is I, *cf.* Table I, b.p. 111–113° and the yield is stated to be 44%. In addition to I, three other fluorinated materials have been recovered, their properties are listed below.

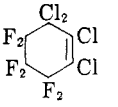
TABLE I

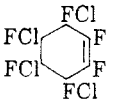
Compound	B.P.	d_4^{20}	n_D^{30}	Analyses		Yield, %
				Theor.	Found	
 (I)	113°	1.729	1.3653	Cl 24.05	24.23	20–30
 (II)	140–1.8°	1.767	1.3995	Cl 34.10 C 23.11	33.71 24.07	20
 (III)	95°/63 mm.	1.793	1.4313	Cl 43.30 C 22.02	42.70 23.18	5
 (IV)	89–90°	1.642	1.3619	Cl 29.0	28.43	<1%

The purity of compounds I–III was checked by gas chromatography and structure determinations were made with the aid of infrared and nuclear magnetic resonance[2] measurements.

The following basis was used for structural assignments. In compounds I–III a single infrared absorption band was found at 6.15 μ and was assigned to the CCl=CCl grouping. Compounds with F atoms attached to the doubly bonded carbon atoms absorb at higher frequencies as has been observed with a number of compounds. The NMR absorption for I shows two different kinds of F atoms in agreement with the formula assigned and oxidation with $KMnO_4$ gives the expected perfluoroadipic acid.[1] The compound II was shown to have four different kinds of F atoms and the boiling point, refractive index, and density show the proper incremental changes.

The highest boiling material (III) was assigned the structure shown since NMR indicates three types of fluorine each containing two F atoms. Other structures for III which are unlikely but cannot be ruled out by NMR are as follows:


A


B

In both of these cases one would expect to find a signal very near the high field reference line from either C=CF or CF_2—CF_2—CF_2 groupings. However, the 6.15μ CCl=CCl band definitely rules out structure B.

Also isolated was a very small amount of IV.[3] Further identification was made by chlorinating this material under the influence of ultraviolet light to give a solid m.p. 138–145°, Cl 43.4%. The reported product of the chlorination is $C_5F_6Cl_4$, m.p. 151°, Cl 44.9%. Comparison of the infrared spectrum of IV with the authentic $C_5F_6Cl_2$ was also in agreement.

It was first assumed that the source of IV was the presence of a cyclopentene impurity in the starting material. An examination was made for impurities in the starting C_6Cl_6 by extraction with

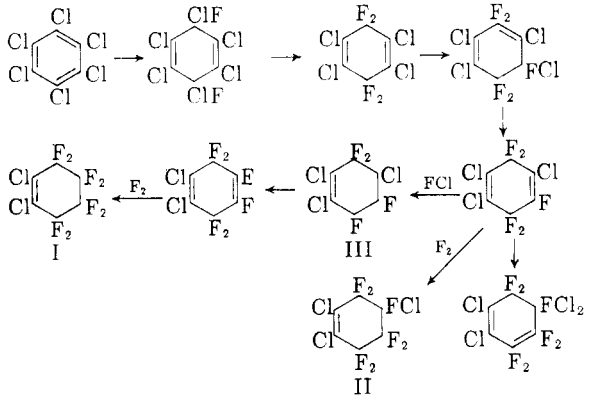
(1) E. T. McBee, P. A. Wiseman, and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

(2) Performed by Varian Associates, Palo Alto, Calif.

(3) A. L. Henne and W. J. Zimmerschied, *J. Am. Chem. Soc.*, **67**, 1265 (1945).

boiling CCl_4. The undissolved residue was discarded and the filtrate partially evaporated to deposit C_6Cl_6 on cooling. An infrared spectrum was run on this filtrate using a pure saturated solution of C_6Cl_6 in CCl_4 as a balance and unknown bands were found at 6.92 (m), 7.15 (s), 7.52 (m), 7.75 (w), 8.55 (m), 8.96 (w), 9.22 (w), 9.43 (w), and 14.71μ(s). An authentic sample of C_6Cl_5H in CCl_4 gave bands at 7.15 (s), 7.48 (s), 7.65 (w), 8.16 (w), 8.28 (w), 8.55 (s), 9.22 (m), and 14.68μ (s). Spectra were run of hexachlorocyclopentene and octachlorofulvene but neighter of these matched the unknown lines. Characteristic bands of octachlorocyclopentene listed in the literature[4] were also absent from this spectra. Therefore, at least one of the impurities present is C_6Cl_5H with still smaller amounts of other materials. The mechanism of the formation of IV is not known but must must come from a benzene starting material.

A mechanism for the formation of the cyclohexene compounds is shown below and is based on the usual addition-elimination mechanism found in fluorination. The conjugation of the double bond is similar to that suggested by Latif[5] in connection with the fluorination of octachlorocyclopentene.



During the initial phase of the fluorination, there will be relatively little Cl present, but as more and more SbF_3Cl_2 is produced there will be a sufficient amount present to allow chlorination of the starting material to produce $C_6F_6Cl_4$. This is the basis for the FCl addition to the intermediate $C_6F_6Cl_2$. In these reactions it is not known whether FCl or F_2 is added as a unit or by a stepwise mechanism involving SbF_4 + F and SbF_3Cl + Cl and no differentiation is made.

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(4) H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 307 (1958).
(5) K. A. Latif, *J. Indian Chem. Soc.*, **30**, 525 (1953).

Synthesis of Isotopically Labeled Medicinals. II. 2-Benzylimidazoline-2-C^{14} Hydrochloride

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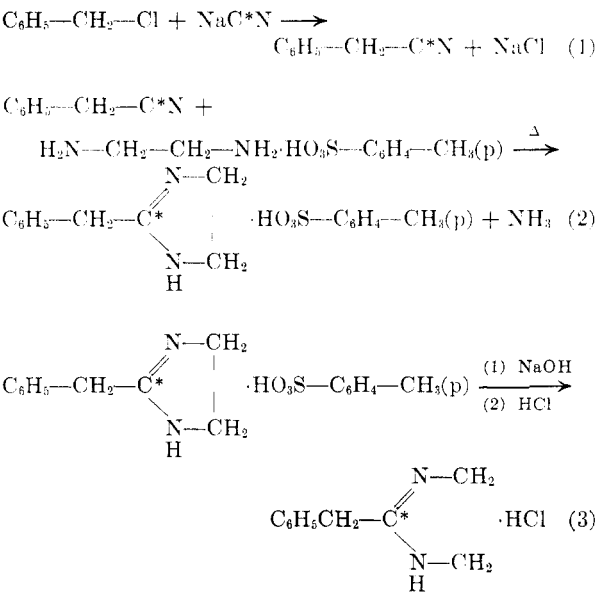
2-Benzylimidazoline hydrochloride[1] is an effective peripheral vasodilating agent and adrenergic blocking agent. A sample of this substance labeled with carbon 14 was required for fate studies in the mammalian body. Although it is manufactured commercially by the condensation of benzyl cyanide and ethylenediamine base in the presence of carbon disulfide, this reaction proved to be unsuitable in our hands on a 10-mmol. scale; only dark colored oils yielding little or none of the desired product were obtained. The modification of Oxley and Short[2] (use of ethylenediamine as the mono-*p*-toluenesulfonate) was finally employed successfully on a micro scale. The complete synthesis took the following form.



Details of the fate of this labeled 2-benzylimidazoline hydrochloride in the rat have been published elsewhere,[3] although it was erroneously stated in that publication that the compound bore the carbon 14 label at the methylene group between the benzene and imidazoline rings.

As is customary, the synthesis was worked out in detail using inactive sodium cyanide before making the target run using the labeled sodium cyanide. Since our sample of labeled sodium cyanide contained sodium hydroxide to minimize loss of the

(1) Tolazoline CIBA = Priscoline^R.
(2) P. Oxley and W. F. Short, *J. Chem. Soc.*, 497 (1947).
(3) B. Century, *Proc. Soc. Exptl. Biol. Med.*, **92**, 518 (1956).