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SYNTHESIS OF SOME BENZIMIDAZOLES CONTAINING 2-PERFLUORO SUBSTITUENTS

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SUMMARY

A new method is described for the preparation of 2-perfluoroalkylether-benzimidazoles through the N-monoacyl derivatives of o-phenylenediamine. 2-Pentafluorophenylbenzimidazole has been obtained by the reaction of o-phenylenediamine and pentafluorobenzoic acid in the presence of polyphosphoric acid. 2-Perfluoroalkylbenzimidazoles have been prepared in excellent yields by direct condensation of o-phenylenediamine with perfluoroalkanecarboxylic acids in the absence of any solvent or added reagent. Some derivatives of these compounds are also described.

INTRODUCTION

A number of 2-perfluoroalkylbenzimidazoles have been previously reported. They were prepared by a) condensation of substituted o-phenylenediamines with perfluorocarboxylic acids in the presence of strong acids [1], b) reduction of the nitro group of N-(o-nitrophenyl) perfluoroalkylamides to the amine and concurrent cyclization to the benzimidazole [1], and c) condensation of CF_3CO_2H or $C_2F_5CO_2H$ with substituted o-phenylenediamines in the absence of mineral acids [2].

In our continuing studies on fluoroalkyl substituted heterocyclic compounds, we have examined the synthesis and reactions of 2-substituted perfluoroalkyl, perfluoroalkylether, as well as perfluoroaryl benzimidazoles. Our findings are described here along with the synthesis of some N-substituted 2-perfluoroalkylbenzimidazoles.

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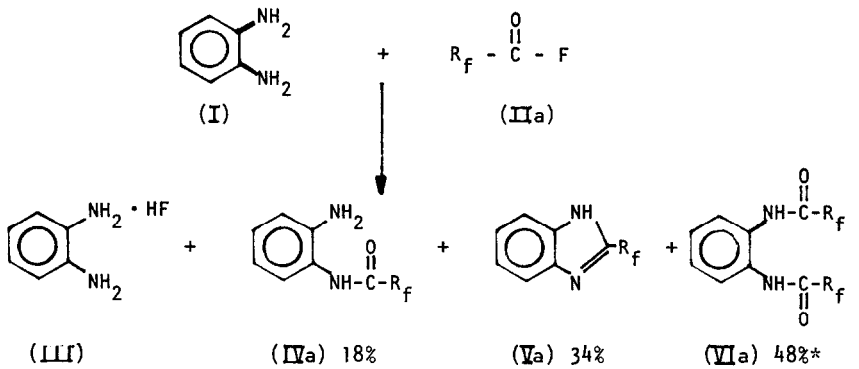
RESULTS AND DISCUSSION

Reaction of equimolar amounts of o-phenylenediamine (I) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ (IIa) in benzene at room temperature for 4 h gave a misture of products (see Scheme 1).



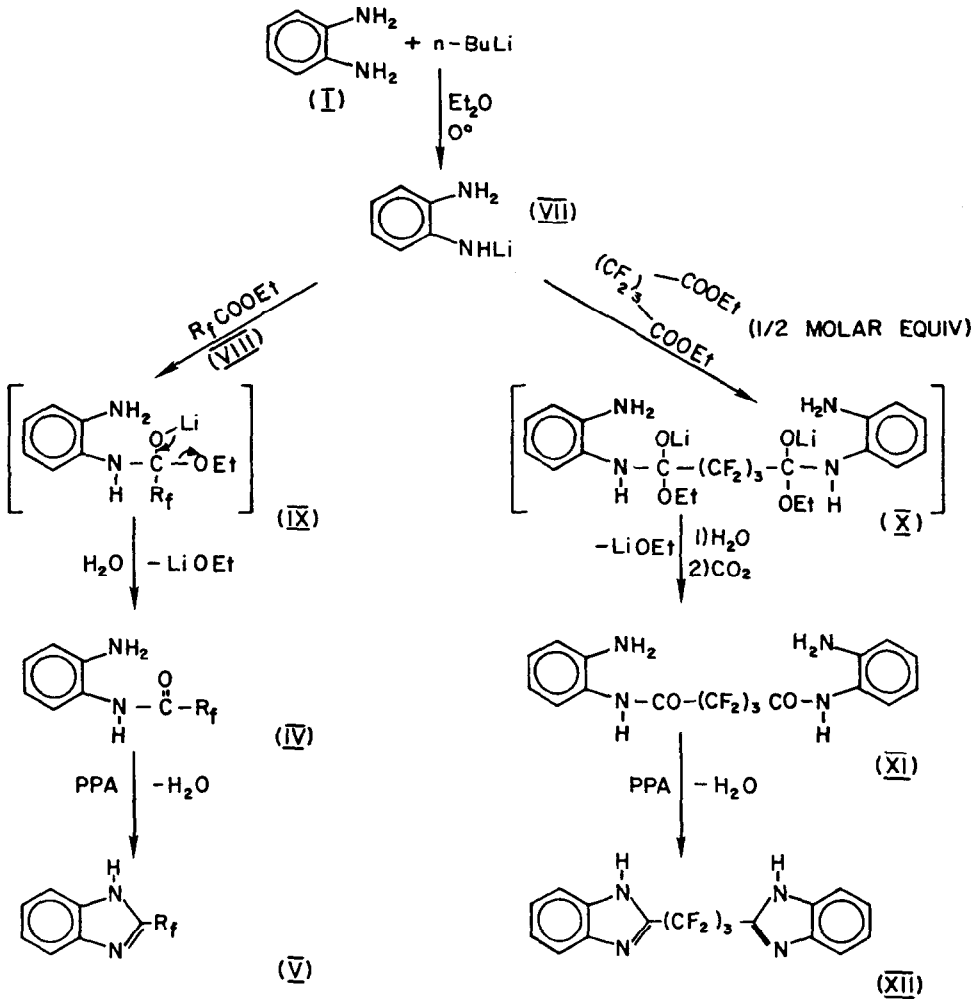
(a) $R_f = -CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

* Identified by GLC/MS only

SCHEME 1

Nearly 50mole % of the starting diamine was converted to the water soluble HF salt (III). The other products consisted of approximately 18% of the monoamide (IVa), 34% of the benzimidazole (Va) and 48% of the diamide (VIa). The reaction mixture, on standing at room temperature for a period of time (∿18 h) led to almost complete cyclization of IVa to Va apparently due to the traces of HF present in the reaction mixture. Repetition of the reaction with a 2:1 molar ratio of the diamine and acid fluoride gave a different product ratio. In addition to the diamine hydrofluoride, the product consisted of approximately 11% of IVa, 73% of Va and 16% of VIa when analyzed at the end of 4 h of reaction. From this reaction, it was possible to isolate a pure sample of Va by column chromatography and repeated crystallization; but its purification was tedious and thus the yield of the 2-perfluoroalkylether-benzimidazole was low.

The 2-perfluoroalkyletherbenzimidazoles could be prepared in excellent yield by a new two-step procedure shown in Scheme 2.



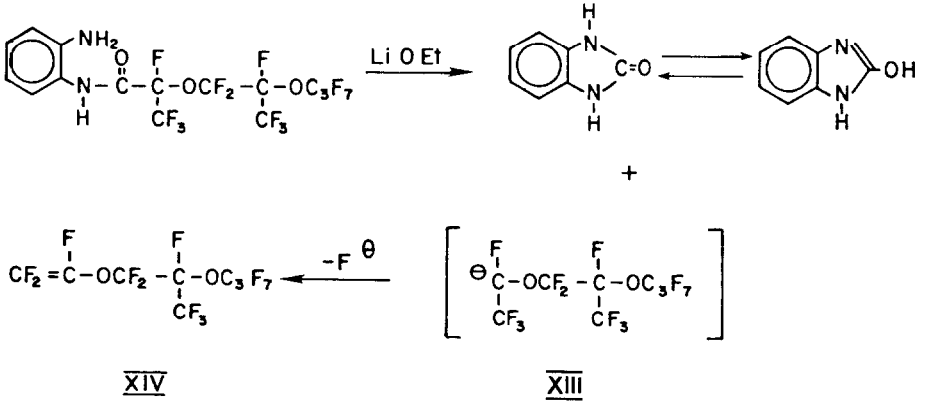
(a) $R_f = -CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

(b) $R_f = -CF(CF_3)\left[OCF_2CF(CF_3)\right]_2 OC_3F_7$

SCHEME 2

This method had general applicability and provided the capability of isolating monoamides of o-phenylenediamine (IV) which was difficult to prepare by other reported methods. The method involves monolithiation of o-phenylenediamine in diethyl ether with n-C_4H_9Li at 0°C, followed by reaction with an alkyl-ester of perfluoroalkylethercarboxylic acid. The metallation appeared to be fast while the reaction with ester was slow and took 5-7 days at room temperature for complete utilization of the ester. The monoamides IVa and IVb and the bis-monoamide XI could be isolated in good yields if the reaction is terminated after one day when the optimum amount of amide was noticed by GLC analysis. The amides could be conveniently cyclized in 75-97% yields to the benzimidazoles by heating with polyphosphoric acid.

During the preparation of the monoamides IVa and IVb, the formation in small amounts of a new volatile product was observed by GLC analysis of the reaction mixture, which was suspected to be formed from the amide and lithium ethoxide generated during the reaction. In order to study this further, IVa and lithium ethoxide were reacted in diethyl ether at room temperature. The reaction was slow as indicated by the recovery of about 75% of the starting amide after 3 days of reaction. The same volatile product as well as 2-hydroxybenzimidazole were isolated from the reaction mixture. The reaction apparently involves the formation of the anion XIII which eliminates a fluoride ion giving the olefin XIV as shown in Scheme 3. Though the volatile component was not completely chracterized, its mass spectrum analysis corresponded to that of the olefin XIV.



XIV XIII

SCHEME 3

This decomposition is analogous to the decomposition of fluorinated esters with NaOR [3] and $LiOC_2H_5$[4]. It would appear that this may be a general mode of decomposition exhibited by many different derivatives of perfluoroalkyl or perfluoroalkylethercarboxylic acids in the presence of bases.

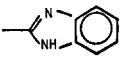
2-Pentafluorophenylbenzimidazole (XV) was best prepared in >90% yield by heating o-phenylenediamine with pentafluorobenzoic acid and polyphosphoric acid at 190-200°C for 4 h. The presence of polyphosphoric acid was not helpful in the synthesis of 2-perfluoroalkylbenzimidazole. For instance, when o-phenylenediamine and $C_3F_7CO_2H$ were heated together with excess polyphosphoric acid at 120°C for 12 h, less than 10% yield of 2-heptafluoropropylbenzimidazole could be obtained. When polyphosphoric acid was omitted from this reaction, a 90% yield of 2-heptafluoropropylbenzimidazole was obtained by heating the reactants at 115-120°C for 4 h. The temperature at which the reaction was conducted appeared critical as the same reaction carried out at 100-105°C for about 6 h gave only about 15% yield of the benzimidazole.

Instead of the perfluoroalkanecarboxylic acid, the anhydrides could also be used. Heating $[C_2F_5C(O)]_2O$ with o-phenylenediamine at 110-120°C for 4 h gave 2-pentafluoroethylbenzimidazole in 88% yield.

The thermal decomposition of some of the new benzimidazoles prepared as well as some known benzimidazoles were determined by heating them under vacuum in sealed pyrex glass tubes and estimating the undecomposed amounts by quantitative gas chromatography using n-dodecane as an internal standard. The data are presented in Table 1.

TABLE 1

THERMAL DECOMPOSITION* OF 2-SUBSTITUTED BENZIMIDAZOLES

2-SUBSTITUENT	M.P.(°C)	AMOUNT DECOMPOSED (%)		
		200°C	250°C	325°C
-H	170	--	6·4	28·3
-OH	310-2	--	NIL	--
	300-1	--	4·0	9·0
	226	--	∿100	--
$-\underset{CF_3}{\overset{1}{C}}FOCF_2\underset{CF_3}{\overset{2}{C}}FOC_3F_7$	116	36·8	45·8	--
$-(CF_2)_3$ 	312-4	--	NIL	∿100

* Estimated by determining amount recovered by GLC using n-dodecane as internal standard after heating sample in an evacuated sealed pyrex glass tube for 19 h.

Though the data is insufficient to make accurate generalizations, some conclusions can be made. The results indicate that a perfluorinated substituent at the 2-position of the benzimidazole ring tend to decrease its thermal stability. It also suggests that an aliphatic perfluorinated substituent has greater thermal stability than a perfluorophenyl substituent.

Benzimidazoles are known to form N-metal salts with various metals. 2-Phenyl and 2-methylbenzimidazoles were reported to form silver and mercury salts while no salt formation was noticed with copper, cadmium, cobalt or zinc [5,6]. We have observed that 2-pentafluoroethylbenzimidazole forms a copper salt when refluxed in anhydrous ethanol with cuprous oxide. Though the exact structure of the copper salt was not determined, its elemental analysis corresponds to a specie formed by displacement of the amino hydrogen with one copper atom.

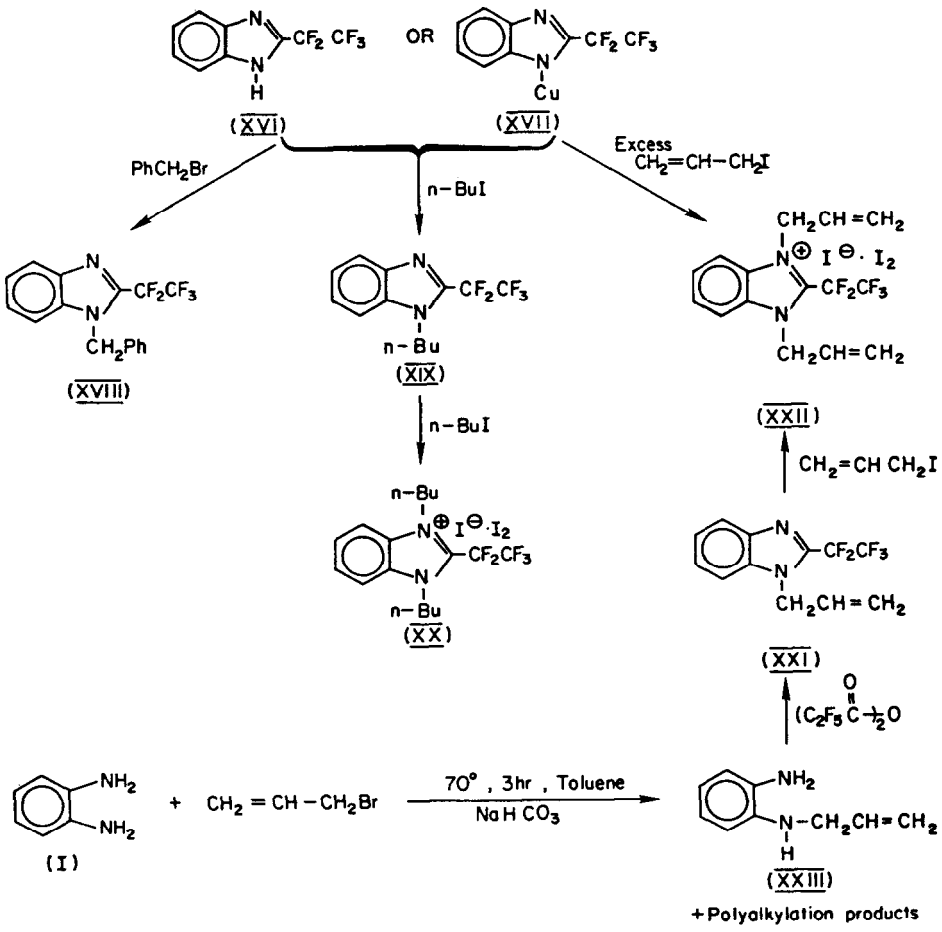
The free benzimidazole as well as the copper salt reacted with an excess of alkyl halides like $C_6H_5CH_2Br$, $n\text{-}C_4H_9I$ and $CH_2 = CHCH_2I$ in the absence of any solvents and under reflux to give well-defined products (See Scheme 4) which could be isolated and characterized. With $n\text{-}C_4H_9I$, the derivative XIX initially formed, reacted further with $n\text{-}C_4H_9I$ and the I_2 liberated in the reaction medium to yield a periodide (XX). These products could be preferentially isolated by controlling the reaction time. With allyl iodide, XXI and the periodide (XXII) could be isolated. The N-allyl derivative XXI was also prepared by an alternate procedure by heating N-allyl-o-phenylenediamine (XXIII) (obtained by alkylation of o-phenylenediamine with $CH_2 = CHCH_2Br$) with $[C_2F_5C(O)]_2O$. Heating XXI with excess $CH_2 = CHCH_2I$ also gave the periodide XXII. Under these conditions $n\text{-}C_4H_9Br$ or $n\text{-}C_7H_{15}I$ did not react with XVII, while $CH_2 = CHCH_2Br$ gave a complex mixture of products. Formation of periodides have been reported in the reaction of 2-methylbenzimidazole with methyl iodide [7].

The analytical data of all new compounds prepared are given in Table 2.

The thermal decomposition of the periodide XXII was studied by mass spectral thermal analysis. The volatile products identified were composed of $CH_2 = CHCH_2I$ and I_2 released between 73°C and 135°C. Most of the other ion peaks were consistent with fragmentation of N-allylbenzimidazole XXI.

EXPERIMENTAL

Most of the new compounds prepared were characterized by mass spectral (chemical ionization), infrared and elemental analysis. GLC analysis were performed on a Perkin-Elmer Sigma 1 or Hewlett-Packard Model 700 instrument



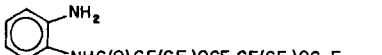
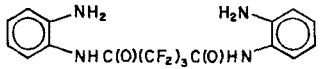
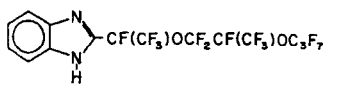
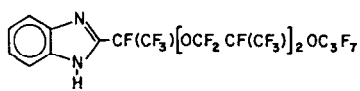
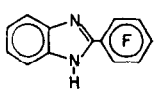
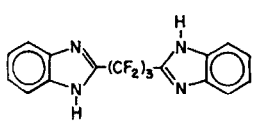
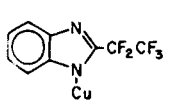
using a 6' or 12' stainless steel (1/4" I.D.) column packed with 10% SE30 or Apiezon L on Chromosorb W. Details of the new compounds prepared are recorded in Table 2.

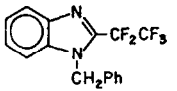
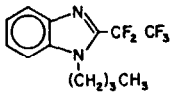
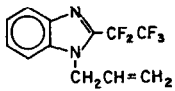
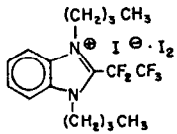
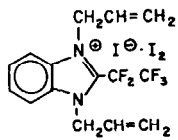
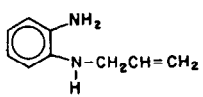
Acylation of o-phenylenediamine (I) with $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$(IIa)

To a solution of I (1.08g; 0.01mole) dissolved in benzene (60ml) under nitrogen and rapid stirring was added IIa at room temperature over a period of 5 min. A white precipitate was slowly formed. The mixture was stirred for 4 h after which diethyl ether (60ml) was added which precipitated the amine hydrofluoride (III). The precipitate III (0.50g) was filtered and the solvents and low boiling components removed on a rotary vacuum evaporator.

TABLE 2

Analytical Data of New Compounds Prepared

Compound		m.p.(b.p.)°C	MS calc./found	Elemental analysis C calc./found	H calc./found	N calc./found	
	[IVa][1]	78-79	586/586	30.70/30.82	1.19/0.98	4.78/4.80	
	[XI][1]	—[2]	420/420	48.57/48.43	3.33/3.31	13.33/12.85	
	[Va]	116	568/568	31.69/31.85	0.88/0.86	4.93/4.87	
	[Vb]	89-90	734/734	29.43/29.36	0.68/0.43	3.81/3.92	
	[XV]	225-226	284/284	54.93/54.72	1.76/1.46	9.86/9.63	
	[XII]	312-314	384/384	53.13/53.28	2.60/3.00	14.58/13.84	
	[XVII]	—[3]	--	36.18/35.84	1.34/1.25	9.38/9.78	21.27/20.81[4]

	[XVIII]	101-102	326/326	58.89/58.91	3.37/3.00	8.59/8.43	
	[XIX]	64/0.1mm	292/292	53.42/53.72	4.45/4.59	9.59/8.99	
	[XXI]	70-71/0.09mm	276/276	52.17/51.88	3.26/2.98	10.15/10.37	
	[XX]	114(dec.)	730/292 $[M^+-C_4H_9I,I_2]$	27.95/27.87	3.01/2.89	3.84/3.77	52.19[5]/51.03
	[XXII]	90-91(dec.)	698/276 $[M^+-C_3H_5I,I_2]$	25.70/25.65	2.00/1.90	4.01/3.91	54.58[5]/53.70
	[XXIII]	74-75/0.08mm	148/148	72.97/72.57	8.11/8.15	19.69/18.92	

1 Shows IR carbonyl absorption at 1700cm^{-1}.
2 Cyclizes to XII on heating.
3 Does not have a sharp m.p.
4 Copper analysis
5 Iodine analysis.

The remaining brown viscous semisolid was analyzed immediately by G.L.C. and indicated the monoamide IVa (18%), benzimidazole Va (34%) and the diamide VIa (48%). On standing at room temperature for a period of 24 h, the monoamide IVa in the crude reaction mixture was almost completely converted to Va. The same reaction, when repeated using a 2:1 molar ratio of I:IIa, gave a higher yield of Va. Isolation of Va by this synthesis procedure is difficult.

Preparation of IVa

To a solution of I (7.56g; 0.07mole) dissolved in anhydrous diethyl ether (400ml) at 0°C was added n-C_4H_9Li (4.48g; 0.07mole) over a period of 20 min. There was a slight temperature rise (4°C) noted and the color of the reaction mixture turned into a deep blue. The ester $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)OC_2H_5$ (VIIIa) was added to the reaction mixture over a period of 20 min. Aliquot samples were removed periodically, hydrolyzed with water and analyzed by G.L.C. to follow the formation of the monoamide IVa. After addition of the ester, the reaction mixture was allowed to warm up to room temperature overnight. Although stirring of the reaction was continued for a total of 5 days, G.L.C. analysis indicated maximum yield of IVa at the end of 24 h. Beyond that period, the amide was slowly consumed by a side reaction (see later) with the $LiOC_2H_5$. The reaction mixture was hydrolyzed by the addition of water, the diethyl ether layer separated and the aqueous layer extracted once with additional diethyl ether. The diethyl ether layers were combined, dried and the solvent removed to yield the crude amide (39.7g; 96%) as a brown solid. Recrystallization (2x) from benzene produced the amide IVa (27.1g; 66%) as a pale cream solid.

Preparation of IVb

The amide IVb was prepared as described above (86% yield). It was a low melting solid and attempts to prepare a pure sample by recrystallization were unsuccessful. The crude IVb was used for cyclization to the benzimidazole Vb (see later).

Preparation of bis-monoamide XI

The bis-monoamide XI was prepared by the method described above using I (12.9g; 0.12mole) and n-C_4H_9Li (7.68g; 0.12mole) and $C_2H_5OC(O)(CF_2)_3C(O)OC_2H_5$ (17.76g; 0.06mole). The reaction was terminated after 20 h during which time a thick yellow precipitate formed. The precipitate (hygroscopic) was filtered off and quickly dissolved in a minimum amount of water and neutralized by passing CO_2 through the aqueous solution. A cream solid formed, was

filtered and washed with water and dried to yield the product XI (17.5g; 83%). The compound was recrystallized from ethanol to yield a white crystalline product. The bis-amide did not have a sharp melting point since it began to cyclize to the bis-benzimidazole XII near its melting point.

Cyclization of monoamides (general procedure)

The monoamide (12.5g) was heated under nitrogen with polyphosphoric acid (~150g) at about 130°C for a period of 3 to 4 h with efficient stirring. Aliquot samples were periodically removed, dissolved in water, extracted with diethyl ether and analyzed by GLC. The reaction was stopped when the amide component in the GLC analysis disappeared. When the reaction was terminated, the mixture was slowly added to ice, the white solid separated by filtration and washed repeatedly with water. It was then stirred with dil. $NaHCO_3$ solution, washed again with water and finally dried to yield the crude benzimidazole. The crude benzimidazoles were further purified by recrystallization from petroleum ether (40-60°C) or by sublimation. By this procedure Va, Vb and XII were obtained in 93%, 74% and 70% respectively.

Reaction of IVa with $LiOC_2H_5$

To $LiOC_2H_5$ (0.52g; 0.01mole) suspended in anhydrous diethyl ether (25ml) was added the amide IVa (5.86g; 0.01mole) with vigorous stirring under nitrogen. Aliquot samples were removed periodically, hydrolyzed with water, extracted with diethyl ether and analyzed by GLC. With time the amide concentration decreased and the formation of a volatile product was noted. At the end of 3 days approximately 25% of the amide IVa had reacted. The reaction flask was connected to a vacuum line and the volatile products separated and condensed into two traps at -78°C. The first trap contained a mixture of diethyl ether and the volatile product while the second trap contained mostly the diethyl ether. From the first trap most of the diethyl ether was removed by distillation. Analysis of the residue by GLC/MS indicated a molecular weight of 432 which corresponds to the olefin XIV. The brown residue left in the reaction flask was stirred with water (20ml). The brown solid was filtered and identified as the unreacted monoamide. The yellow aqueous layer was acidified with dil. HCl, saturated with NaCl and extracted with diethyl ether to yield a small amount of a pale yellow solid. The IR spectrum was identical to that of an authentic sample of 2-hydroxybenzimidazole.

Preparation of XV

The diamine I (21.6g; 0.20mole), $C_6F_5CO_2H$ (42.4g; 0.20mole) and polyphosphoric acid (200g) were vigorously stirred under nitrogen. The reaction was heated between 190°-200°C for 4 h. The reaction mixture became dark and effervescence was noted. The reaction mixture was cooled to 100°C and poured into ice water with vigorous stirring. The light pink solid which separated was filtered, washed with water and stirred with dil. $NaHCO_3$ solution and dried to yield the crude product (52.0g; 91.5%). It was further recrystallized from ethanol to yield a pure product XV, m.p. 225°-226°C.

Preparation of 2-(n-Heptafluoropropyl)benzimidazole

The diamine I (10.8g; 0.10mole) and $n\text{-}C_3F_7CO_2H$ (42.8g; 0.20mole) were heated under reflux at about 120°C for 4 h. The dark violet reaction mixture was cooled, dissolved in ethanol and boiled with activated charcoal and filtered. The ethanol solution on addition to water precipitated the benzimidazole as a pale orange solid (25.7g; 90%). It was further purified by recrystallization from ethanol/water to yield a pure product, m.p. 220°C (lit.[1], m.p. 220°C).

Preparation of 2-Pentafluoroethylbenzimidazole (XVI)

To the diamine I (2.16g; 0.02mole) was slowly added $[C_2F_5C(O)]_2O$ (6.15g; 0.022mole). The reaction mixture was heated under reflux at ∿120°C for 4 h. The contents of the flask solidified to a violet mass. Water was added to the solid mass and stirred vigorously. The solid was filtered and slurried with dil. $NaHCO_3$ solution, filtered and washed with water repeatedly. After drying, the crude benzimidazole (4.15g; 88%) was obtained. Recrystallization from ethanol/water gave white needles, m.p. 213°C (lit.[1], m.p. 212-214°C).

Preparation of XVII

2-Pentafluoroethylbenzimidazole (XVI) (11.0g; 0.047mole) and cuprous oxide (5.43g; 0.038mole) were heated under reflux in anhydrous C_2H_5OH (100ml) under nitrogen. As the reaction proceeded, a pale grey solid began to form. The reaction was continued for 5 days. Even then some curpous oxide remained unreacted as indicated by the deeper color of cuprous oxide. The reaction mixture was filtered, wash repeatedly with ethanol to remove the excess benzimidazole. The residue suspended in diethyl ether and the heavier

cuprous oxide separated by repeated centrifugation. The pale grey solid (8.5g) was dried and the elemental analysis agreed with the N-copper derivative represented by XVII.

Preparation of N-derivatives (general method)

2-Pentafluoroethylbenzimidazole (XVI) or its copper salt (XVII) was used for the preparation of the N-derivatives. A typical procedure was to heat the benzimidazole or XVII (2.0g) with an excess of the alkyl halide (∿10.0g) in the absence of any solvent for a period of time. Reactions with volatile halides were refluxed while those of less volatile halides were heated to ∿100°C. When an alkyl iodide was used the reaction flask was protected from light even though the liberation of I_2 was still apparent. After the reaction, the excess alkyl halide was removed by distillation under vacuum keeping the temperature below the reaction temperature. The residue was dissolved in ethanol and filtered to remove the copper iodide. Most of the ethanol was removed and the liquid product fractionated or when the product was a solid, it was precipitated by addition of petroleum ether or hexane. The experimental details for the preparation of the various N-derivatives are indicated in Table 3.

Preparation of XXIII

To a mixture of I (21.6g; 0.20mole) dissolved in toluene (350ml) and $NaHCO_3$ (10.0g) was added allyl bromide (5.0g; 0.040mole) over a period of 10 min. The reaction mixture was then heated to 70°C. Aliquot samples were periodically removed and analyzed by GLC which indicated the formation of a number of products. GLC/MS analysis of these products indicated mono, di and polyallyl derivatives were being formed. The reaction was terminated after 2 h, cooled, diluted with ethanol and filtered to remove inorganic salts. The solvent was removed by vacuum which left a dark brown resinous solid. This was added to diethyl ether (100ml) and filtered to remove unreacted I. The diethyl ether solution was evaporated to about 20ml and additional I precipitated by the addition of petroleum ether. The petroleum ether solution was separated and subjected to vacuum distillation which left a red-brown liquid (4.2g) which still contained some unreacted I as indicated by GLC analysis. The mixture was separated by column chromatography (silica gel; petroleum ether eluent) to yield crude N-allyl-o-phenylenediamine XXIII. On distillation, pure XXIII, b.p. 74°-75°C/0.08mm, 1.8g (30% based on $CH_2=CHCH_2Br$) was obtained.

TABLE 3

Preparation of N-substituted Benzimidazoles

Amounts/Reactants							
XVI	XVII	Alkyl Halide	Temp. (°C)	Time	Product	Solvent for Crystallization	Yield(%)
--	2.0g	$PhCH_2Br$ (10.0g)	∿100°	1 Day	XVIII	pet-ether	53
1.0g	--	$PhCH_2Br$ (5.0g)	∿90°	28 h	XVIII	pet-ether	58
--	2.0g	$CH_2=CH-CH_2I$ (10.0g)	60-70°	3 Days	XXII	EtOH-Et_2O-Hexane[1]	30
--	5.0g	$CH_2=CH-CH_2I$ (15.0g)	60-70°	1 Day	XXI	--	50
1.0g	--	n-BuI (5.0g)	70-80°	11 Days	XX[2]	EtOH-Et_2O-Hexane[1]	10
--	2.0g	n-BuI (10.0g)	70-80°	7 Days	XIX[2]	--	24

1 The solvent was 10% EtOH in Et_2O to which excess hexane was added to precipitate the product.

2 Product XIX or XX was also present in these reaction, but was not isolated.

Cyclization of XXIII to XXI

The XXIII from above (1.2g) was mixed with $[C_2F_5C(O)]_2O$ (3ml) and heated in an atmosphere of nitrogen at 100°C for 2 h at which time GLC analysis indicated complete cyclization. The crude reaction mixture was heated under vacuum to remove excess anhydride, the residue was dissolved in diethyl ether, washed with dil. $NaHCO_3$ and water. The diethyl ether layer was dried, solvent removed to yield crude XXI (1,8g; 80%). The crude product was distilled under vacuum to yield XXI, b.p. 70°-71°C/0.09mm as a pale yellow liquid. This compound was identical to XXI obtained from XVII and allyl iodide (see Table 3, 1 day reaction time).

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