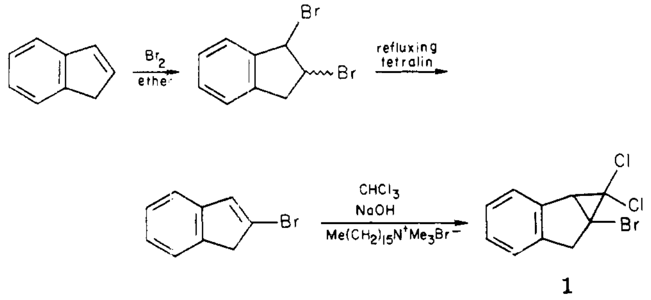
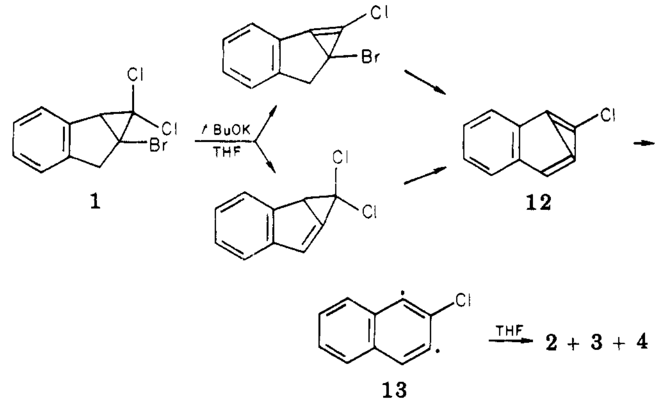
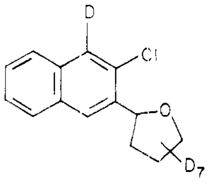
Scheme I



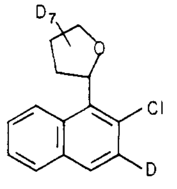
Scheme II



of the label in compounds 3 and 4, the incorporation of eight deuterium atoms (mass spectroscopy) suggests structures 3a and 4a. The remaining products, 5–11, were not deuterated.



3a

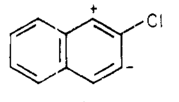


4a

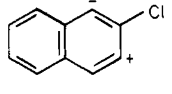
The introduction of deuterium into the chloronaphthalene and the detection of 3 and 4 helps to establish the intermediacy of the diyl 13. The formation of 2, 3, and 4 can then be rationalized by assuming one (or both) of the paths in Scheme II.

The origin of compounds 5–11 is puzzling. However, several control experiments show that all of the products are stable to the reaction conditions. Furthermore, no incorporation of deuterium is detected when the crude reaction mixture or the individual products are treated with t-BuOK in THF-d_8.

We tend to discount zwitterions 15 and 16 as viable



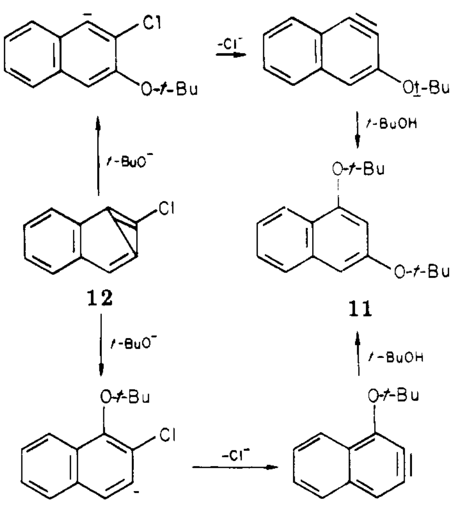
15



16

intermediates to 5–11 since they are probably much less stable (higher energy) than the diyl 13. A possible route to 5–11 is the nonregiospecific addition of nucleophile (Cl^-, Br^-, t-BuO^-) to the bridging bond of 12. This process would lead directly to products 5–10, whereas 11 could arise via one (or both) of the naphthalynes illustrated in Scheme III.

Scheme III



Thus, some ambiguity still exists with regard to the origin of the products which result from incorporation of nucleophile. However, it seems clear that diradical 13 is implicated as an intermediate in the formation of 2–4. The contrasting properties of the parent compound[3] and the naphthalene derivative observed here also await explanation.

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation and Eli Lilly and Company for support of this work.

Registry No. 1, 71436-63-0; 2, 91-58-7; 3, 71436-64-1; 4, 71436-65-2; 5, 2050-69-3; 6, 2050-75-1; 7, 71436-66-3; 8, 71436-67-4; 9, 71436-68-5; 10, 71436-69-6; 11, 71436-70-9; indene, 95-13-6; 2-bromoindene, 10485-09-3.

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Copper-Catalyzed α Addition of Perfluoroalkyl Iodides to Isocyanides

Summary: α Addition of perfluoroalkyl iodides to isocyanides (alkyl or/aryl) affords perfluoroalkylimidoyl iodides in good yield; the addition is catalyzed by copper powder.

Sir: Insertion of divalent carbon species into the carbon–iodine bond of a perfluoroalkyl iodide (R_FI; $R_F = CF_3(CF_2)_n$) is a very unusual reaction. This condensation failed with dichlorocarbene, diazo ketones, and diazo esters and was only achieved with diazomethane, giving a mixture of mono and bis homologation products.[1,2] Furthermore,

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(1) Hudlicky M.; König, J. *Collect. Czech. Chem. Commun.* **1963**, *28*, 2824–2826.

(2) Knunyants, I. L.; Pervova, E. Ya., *Bull. Acad. Sci. USSR (Engl. Transl.)* **1965**, 860–861.

0022-3263/79/1944-4219$01.00/0

Table I

R	mol % isocyanide (1a)	% yield[b] 3
n-butyl	1.3	90
tert-butyl	1.5	70
cyclohexyl	1.2	87
benzyl	2.0	32
2,6-dimethylphenyl	1.0	52

[a] Per 1 mol of $C_6F_{13}I$. [b] Calculated from $C_6F_{13}I$.

insertion of isocyanides into metal–perfluoroalkyl bonds is not known to occur.[3]

We describe here the smooth copper-catalyzed addition of R_FI (1) to isocyanides 2, leading to the formation of perfluoroalkylimidoyl iodides 3.

$$\underset{1}{R_FI} + \underset{2}{C{=}NR} \rightarrow \underset{3}{R_F(I)C{=}NR}$$

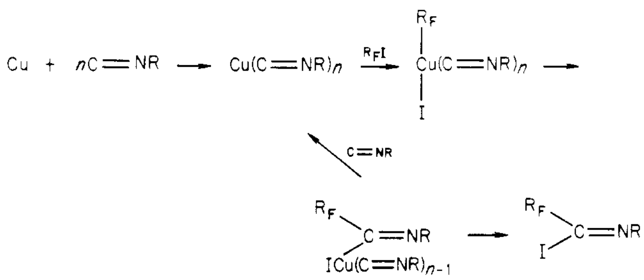
Compounds 3 show an IR absorption band at 1690 cm^{-1} in CCl_4 and a ^{19}F NMR signal at +109 ppm from $CFCl_3$.

This reaction was observed with variable perfluoroalkyl chain length and with alkyl or aryl isocyanides. The yields are approximately the same with $R_F = C_4F_9$, C_6F_{13}, and C_8F_{17}. Table I lists the results obtained with $C_6F_{13}I$. The use of solvent and oxygen- or moisture-free conditions is not necessary. Addition of 0.1 equiv of copper powder to a mixture of R_FI and alkyl isocyanide produces an exothermic reaction. After 2 h, the unchanged copper is eliminated by filtration and the imidoyl iodide is distilled under reduced pressure. With the less reactive 2,6-dimethylphenyl isocyanide, it is necessary to heat the mixture 3 h in benzene in order to increase the rate of the reaction.

The addition is not inhibited by the presence of a radical inhibitor such as diphenylpicrylhydrazyl. It appears that the reaction does not proceed by a radical chain mechanism.[4]

It is well known that metals of columns Ib and IIb, and their derivatives, form complexes with isocyanides.[5] However, we have observed that Zn, $ZnCl_2$, $CuCl_2$, Cu_2O, and $CdCl_2$ do not catalyze the R_FI addition. Apart from copper, silver powder induces a slow reaction with the most reactive cyclohexyl isocyanide (10% conversion after 1 week at room temperature).

Scheme I



On the other hand, it has been shown that the addition of CF_3I to a platinum complex bearing isocyanide ligands occurs on the metal and not on the ligand.[6]

The addition order of reagents is crucial to induce the reaction. It is quite strange to observe that a preformed $Cu(C{=}NR)_m$ complex obtained by heating copper powder and isocyanide does not react with R_FI. Perhaps this difference could be due to the fact that the number of isocyanide ligands is higher in the preformed complex, at the equilibrium, than in the complex formed in situ during the reaction ($m > n$). Oxidative addition of R_FI onto the $Cu(C{=}NR)_n$ complex could be followed by a rearrangement leading to the imidoyl iodide[7] (see Scheme I).

Imidoyl iodides 3 can yield perfluoroacid derivatives (amides, esters, amidines, imidates,...) by hydrolysis or nucleophilic substitution. Owing to the hydrophobic properties of the perfluoroalkyl chains, these compounds are potential tensioactive agents.[8]

Registry No. 1 ($R_F = C_6F_{13}$), 355-43-1; 2 (R = *n*-butyl), 2769-64-4; 2 (R = *tert*-butyl), 7188-38-7; 2 (R = cyclohexyl), 931-53-3; 2 (R = benzyl), 10340-91-7; 2 (R = 2,6-dimethylphenyl), 2769-71-3; 3 (R_F = C_6F_{13}; R = *n*-butyl), 71786-12-4; 3 ($R_F = C_6F_{13}$; R = *tert*-butyl), 71786-13-5; 3 ($R_F = C_6F_{13}$; R = cyclohexyl), 71786-14-6; 3 (R_F = C_6F_{13}; R = benzyl), 71786-15-7; 3 ($R_F = C_6F_{13}$; R = 2,6-dimethylphenyl), 71786-16-8; Cu, 7440-50-8.

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(3) Treichel, P. M.; Hess, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 4731–4733.

(4) In the case of the most reactive isocyanides a radical chain addition can be performed thermally, without copper. This reaction is inhibited by diphenylpicrylhydrazyl. The thermal addition failed with the less reactive 2,6-dimethylphenyl isocyanide and *tert*-butyl isocyanide.

(5) Saegusa, T.; Ito, Y. *Synthesis*, **1975**, 291–300.

(6) Larkin, G. A.; Mason, R.; Wallbridge, M. G. H. *Chem. Commun.* **1971**, 1054–1055

(7) The reaction of R_FI is very different from that of usual alkyl halides; allylic and benzylic halides react with a molar quantity of the copper isocyanide complex to give coupling products and copper halide: Ito, Y.; Yonezawa, K.; Saegusa, T. *J. Org. Chem.* **1974**, *39*, 2769–2773. Ballatore, A.; Crozet, M. P.; Surzur, J. M. *Tetrahedron Lett.* **1979**, 3073–3076.

(8) Schuierer, E. *Tenside* **1976**, *13*, 1–5.