Oxidative coupling of radicals in reactions of compounds of tervalent iodine with trimethylsilyl(phenyl)acetylene

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Reactions of trimethylsilyl(phenyl)acetylene with aryl and alkyl difluoroiodides give coupling products of substituents in high yields.

Key words: oxidative coupling, hypervalency, tervalent iodine, trigonal bipyramid.

The interest in the oxidative coupling of ligands at hypervalent nonmetal atoms¹⁻⁴ is caused by the similarity of these transformations with those observed in widely known reactions catalyzed by transition metal complexes.

In order to determine the effect of the electronic structure of substituents on the direction of coupling we studied the reactions of aryl and alkyl difluoroiodides RIF_2 (1) with trimethylsilyl(phenyl)acetylene (2) in the presence of catalytic amounts of KF and 18-crown-6 as activators of silylacetylene 2 (Scheme 1).

Scheme 1

$$RIF_{2} + 2 Me_{3}SiC = CPh \qquad \frac{CH_{2}CI_{2}}{KF, 18-crown-6}$$

$$R = C_3 F_7$$
 (a), $C_6 F_5$ (b), Ph (c), Me (d)

The reaction proceeds almost quantitatively, and the composition of the products depends substantially on the type of the radical R (Table 1). The ratio of products **4** (duplication of PhC=C radicals) and 5a-d (coupling of PhC=C and R) varies from 1 : 5.7 for 1a to 3.25 : 1 for 1b, and the selectivity of the formation of product 5a reaches 85 %.

Compounds of three-coordinate iodine have the structure of a trigonal bipyramid in which substituents can occupy the apical (a) (which is typical of the most electronegative groups) or equatorial (e) positions; it is

 Table 1. Relative molar content of duplication products

R	4	5a-d	6
C_3F_7 (a)	1	5.7	5.7
$C_{6}F_{5}(b)$	3.25	1	1.25
Ph (c)	1.84	2.25	1.77
Me (d)	2	1	9

considered that coupling of the a-e-substituents occurs.¹

In our case (see Scheme 1), an intermediate compound can have the structure A or B.

$$\begin{array}{c} C \equiv C - Ph (a) \\ \hline R (e) \\ C \equiv C - Ph (a) \end{array} \qquad \begin{array}{c} A \\ R \\ \hline R \\ C \equiv C - Ph \\ B \end{array} \qquad \begin{array}{c} R \\ I - C \equiv C - Ph \\ C \equiv C - Ph \\ B \end{array}$$

The formation of considerable (and sometimes predominant) amounts of diphenyldiacetylene 4 attests to the fact that the intermediate compound has the structure **B** (or a low barrier to the transition $\mathbf{A} \Leftrightarrow \mathbf{B}$).

It is highly probable that the selectivity of the reaction of radical coupling can be considerably increased by changing the nature of the central atom (for example, using Se^{IV}, Te^{IV}, or Bi^V halides) or by changing substituents at the central atom or, *e.g.*, including the substituent into the cycle. Work in this direction is in progress.

Experimental

The initial difluoroiodides 1a-d were obtained by the known procedures.⁵ Reaction mixtures were analyzed by GLC on a Chrom-5 chromatograph using stationary phases SE-30

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 1022-1023, April, 1996.

1066-5285/96/4504-0977 \$15.00 © 1996 Plenum Publishing Corporation

and XE-60. ¹H and ¹⁹F NMR spectra were recorded on a Bruker CXP-200 spectrometer relative to $SiMe_4$ and CF_3COOH , respectively.

General procedure. A solution of difluoride 1a-d $(4 \cdot 10^{-4} \text{ mol})$ in dry CH_2Cl_2 (4-5 mL) was mixed with thoroughly dried KF $(1 \cdot 10^{-4} \text{ mol})$ and 18-crown-6 $(1 \cdot 10^{-4} \text{ mol})$. Then acetylene 2 $(8 \cdot 10^{-4} \text{ mol})$ was added dropwise with stirring and cooling with ice water. The mixture was stirred for 0.5 h at ~20 °C and analyzed by GLC. In all cases, only trace amounts of the initial acetylene 2 were observed in the reaction mixture, which indicates that the reaction was quantitatively. If necessary, the products were isolated by column chromatography (5a,b) on SiO₂ or by preparative GLC.

Products **4** ⁶ and **6** ⁷ were synthesized by the known procedures. **5a**. ¹H NMR, δ : 7.46 (m). ¹⁹F NMR, δ : -2.56 (m, 3 F); -20.5 (m, 2 F); -49.3 (m, 2 F). **5b**. ¹H NMR, δ : 7.42 (m, 2 H); 7.58 (m, 3 H). ¹⁹F NMR, δ : -59.1 (m, 2 F); -76.1 (m, 1 F); -84.6 (m, 2 F).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09073).

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Received December 18, 1995

Acylation of phenols with γ -chlorobutyroyl chloride and transformations of the reaction products

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Alkylphenols afford only *O*-acyl derivatives on treatment with γ -chlorobutyroyl chloride in the presence of both Et₃N and AlCl₃ at 20–60 °C. They cyclize under the action of K₂CO₃ in DMSO into the respective cyclopropanes and undergo Fries rearrangement on heating with AlCl₃ at 120 °C into *C*-acyl derivatives.

Key words: alkylphenols, γ -chlorobutyroyl chloride, O-acylation, cyclopropanes, Fries rearrangement.

Phenol has previously been shown to undergo O-acylation on treatment with γ -chlorobutyroyl chloride (CBC) in the presence of Et₃N. Under Friedel—Crafts conditions (in the presence of AlCl₃), only 4-acyl derivatives are formed from alkoxybenzene and only 2-acyl derivatives are formed from 4-substituted alkoxybenzenes (4-OR, Br).¹ Some reactions of these compounds have been studied.²

In the present work, the *O*-acylation of phenols $(1a-e)^{3-6}$ on treatment with CBC in the presence of Et₃N and subsequent cyclization into cyclopropanes are carried out (Scheme 1).

Compounds 2d,e were also synthesized by the thiylation of O-acyl derivative 2a in the presence of azobis-



Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 1023-1025, April, 1996.