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References and Notes

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Coupling Reaction of 1-Chloro-2-Iodoperfluorocycloalkenes with 2-Chlorohexafluorocyclopentenylcopper Reagent

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Since the coupling of perfluorovinyl iodides with copper bronze was initially reported by Tatlow,¹ the use of copper powder in coupling reaction of 1-chloro-2-iodo- and 1,2-diiodo-perfluorocycloalkenes has been reported by Park *et al.*² to be able to produce coupled product by reductive coupling. In a previous report, the reaction of equal molar quantities of different 1-chloro-2-iodoperfluorocycloalkenes with copper powder was described to give the mixture of a cross-coupled product and self-coupled products.³

A facile synthesis of 2-chlorohexafluorocyclopentenylcopper reagent (**1**)⁴ has prompted our investigation into these coupling reaction. We wish to report a facile synthesis of cross-coupled product by reaction of 1-chloro-2-iodoperfluorocyclopropene (**2**), -cyclobutene (**3**), -cyclohexene (**5**) with the solution of **1** and a high yield of self-coupled product by reaction of 1-chloro-2-iodohexafluorocyclopentene (**4**) with the solution of **1**.

Hitherto inaccessible compound, 2-chloro-1-[1'-(2'-chloro-3',3'-difluorocyclopropenyl)]-hexafluorocyclopentene (**6**), was synthesized by cross-coupling reaction of **2** with the solution of **1** at -30°C in 52% yield. Though the reaction of a few nucleophiles with fluorohalogenocyclopropenes has been investigated,⁵⁻⁷ there has been no report so far on the coupling reaction of fluorohalogenocyclopropenes.

While the reaction of equal molar mixture of **3** and **4** with copper powder gave the mixture of a cross-coupled product and self-coupled products, we could synthesize only a cross-coupled product, 2-chloro-1-[1'-(2'-chlorotetrafluorocyclobutenyl)]-hexafluorocyclopentene (**7**), in 71% yield through treatment of the solution **1** with **3** at -30°C. The only

Table 1. Reaction of 1-chloro-2-iodoperfluorocycloalkenes with **1**^a

1	2 , n = 1	6 , n = 1	
	3 , n = 2	7 , n = 2	
	4 , n = 3	8 , n = 3	
	5 , n = 4	9 , n = 4	
Reactant	Product	Yield ^b %	bp °C (mmHg)
2	6	52	56-58 (80) ⁸
3	7	71	69.5-71 (30)
4	8	90	83-84 (50)
5	9	92	60.5-61 (30)

^a DMF was used as solvent, ^b Isolated yield.

by-product obtained from this reaction in ¹⁹F-NMR spectrum was found to be the reduced product, 1H-2-chlorohexafluorocyclopentene.

When **4** is mixed with the solution of **1** at -30°C, the self-coupled product, 2,2'-dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (**8**), is afforded in 90% yield. The treatment of the solution of **1** with **5** gave the cross-coupled product, 2-chloro-1-[1'-(2'-chlorooctafluorocyclohexenyl)]-hexafluorocyclopentene (**9**), in 92% yield. These results represent considerably higher yield than the one obtainable by the

method previously reported in the literature.²

The following procedure for preparing compound **6** is representative. To a precooled (-30°C) stirred solution of **1** (20 mmol)⁴ was added 20 mmol of **2** slowly, the mixture was maintained at -30°C for 6 hrs with stirring. The reaction mixture was allowed to reach to room temperature. It was then flash distilled and the usual workup afforded product **6**, purified by distillation.

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8. Spectral data of **6**: ^{19}F -NMR spectrum was measured in CDCl_3 . Chemical Shifts are reported in ppm with referenced to CFCl_3 . $-100.8(\text{s}, 2\text{F})$, $-106.9(\text{s}, 2\text{F})$, $-113.5(\text{s}, 2\text{F})$, $-129.6(\text{m}, 2\text{F}, J = 4\text{Hz})$; IR(neat film) 1795 cm^{-1} ($\nu_{\text{C}=\text{C}}$ of cyclopropene), 1615 cm^{-1} ($\nu_{\text{C}=\text{C}}$ of cyclopentene); MS (m/z) 318 (M^+ , 12.3%), 283 ($\text{M}-\text{Cl}$, 100%).

The Effect of Medium on the α -Effect

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The rationalization of nucleophilic reactivity has intrigued chemists since the monumental work of Ingold.¹ Basicity has been most commonly used to correlate nucleophilicity, although recently the vertical ionization energy has also showed good correlations with the nucleophilicity of various types of anionic nucleophiles.² However, abnormally higher nucleophilicity than predicted from the basicity has often observed in the reactions of nucleophiles containing an atom with one or more nonbonding electron pairs adjacent to the reaction center (the α -position). Thus such a type of nucleophiles was termed α -nucleophiles and the enhanced nucleophilic reactivity of the α -nucleophiles was therefore termed the α -effect.³

Many theories have been advanced to explain the cause of the α -effect.⁴ The suggested origins of the α -effect are 1) ground-state destabilization of the α -nucleophile,⁵ 2) transition-state stabilization,⁶ 3) polarizability,⁷ and 4) solvent effects.⁸⁻⁹ However any one of these effects alone does not fully account for the cause of the α -effect. Especially the solvent effect has been the subject of controversy. It has been claimed that in some studies the solvation effect is unimportant as the origin of the α -effect^{8a-d} but other studies,^{9a-b} including theoretical molecular orbital calculations, indicate that solvation should be an important factor.

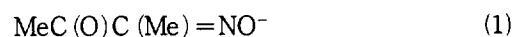
Recently a systematic study has revealed that the solvent effect on the α -effect is very important for the reaction of *p*-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (1) as the α -nucleophile, in comparison with *p*-chlorophenoxide (2) as the corresponding normal nucleophile in dimethyl sulfoxide (DMSO)- H_2O mixtures of varying compositions.¹⁰ We have now studied the same reactions in

Table 1. Kinetic Data for Reactions of *p*-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (1) and *p*-chlorophenoxide (2) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixtures at 25.0°C

mol. % CH_3CN	$k(2)$, $\text{M}^{-1}\text{s}^{-1}$	$k(1)$, $\text{M}^{-1}\text{s}^{-1}$	$k(1)/k(2)$
0	.685 (.685)	65.8 (65.8)	96 (96)
10.0	.385 (-)	37.2 (-)	97 (-)
20.0	.255 (.760)	29.5 (139)	116(183)
30.0	.197 (-)	29.2 (-)	148 (-)
40.0	.198 (2.80)	35.6 (740)	180(264)
50.0	.217 (5.90)	45.6 (1,680)	210(285)
60.0	.266 (13.6)	67.5 (3,850)	254(283)
70.0	.391 (34.7)	122 (8,200)	312(236)
80.0	.712 (94.8)	263 (17,200)	369(181)
90.0	2.12 (334)	943 (40,500)	445(121)

*The data in parentheses are obtained from ref. 10 for the reactions run in $\text{DMSO}-\text{H}_2\text{O}$ mixtures.

various compositions of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixtures to examine whether the previous result is a limited phenomenon only in the $\text{DMSO}-\text{H}_2\text{O}$ system.



In Table 1 are presented the second order rate constants for the reactions of PNPA with (1) and (2). The rate constants decrease gradually as CH_3CN concentration increases