CONCLUSIONS

1. The interaction of ω-haloalkylbenzenechromium tricarbonyl with the metal carbonyl anions $[Fe(CO)_2C_5H_5]^-$ and $[Re(CO)_5]^-$ has been studied and it was shown that the anion $[Fe(CO_2)\cdot C_5H_5]^-$ readily formed binuclear complexes.

2. Partial dehalogenation occurred on interacting alkyl iodides with $[Re(CO)_5]^-$ together with the formation of the appropriate σ complexes. Halogen containing chromium tricarbonyl derivatives reacted with $[Re(CO)_5]^-$ variously depending on the nature of the halogen while under mild conditions one did not react and the other gave exclusively a dehalogenation product.

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TRIFLUOROVINYL DERIVATIVES OF ZINC AND TIN IN THE SYNTHESIS OF TRIFLUOROSTYRENES

R. S. Sorokina, L. F. Rybakova,
I. O. Kalinovskii, and I. P. Beletskaya

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141'161

Trifluorostyrenes are of interest since various derivatives of aryltrifluoroethylenes and also polymers are obtained based on them which possess good dielectric properties and enchanced thermostability [1-3].

However the known methods of synthesis of fluorinated styrenes are unsatisfactory due to low yields. The possibilities of the method of [4] for obtaining pure monomers in sufficiently good yields are limited to derivatives containing substituents unsensitive to the action of reactive organometallic compounds.

In the present work the reactions of $CF_2{=}CFZnCl$, obtained *in situ* from $CF_2{=}CFLi$ and $ZnCl_2$ (1:1), and compounds of type $CF_2{=}CFSnR_3$, with substituted iodobenzenes in the presence of catalytic amounts of PdL_4 or $PhPdIL_2$ complexes where $L = Ph_3P$ have been studied with the aim of developing a convenient method for the synthesis of trifluorostyrenes.

$$CF_2{=}CFZnCl + p\text{-}XC_6H_4I \xrightarrow[\text{THF / ether}, 0^\circ - \sim 20^\circ]{\text{PdL}_4 \text{ or PhPdIL}_2)\ (2\%)} CF_2{=}CFC_6H_4X\text{-}p + ZnClI$$

$X = H$, Me, MeO, Cl.

$$CF_2{=}CFSnR_3 + p\text{-}XC_6H_4I \xrightarrow[60-80^\circ,\ \text{HMPTA}]{\text{PdL}_4 \text{ (or PhPdIL}_2)\ (2-5\%)} CF_2{=}CFC_6H_4X\text{-}p + R_3SnI$$

$X = H$, 1.

L. Ya. Karpov Physicochemical Institute, Moscow. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 7, pp. 1647-1649, July, 1985. Original article submitted March 14, 1984.

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Interest in the use of the indicated organometallic compounds is explained by the following. They are stable at 0°C or above in difference to the corresponding Li derivatives (stable up to −80°C) of [5] and Mg (stable up to −20°C) of [6] and are able to react with iodobenzenes containing functional groups. The reaction of $CF_2{=}CFZnCl$ with PhI in the presence of $PhPdIL_2$ at 20°C led to trifluorostyrene in practically quantitative yield. Replacement of I in p-MeC_6H_4I or $MeOC_6H_4I$ under the action of $CF_2{=}CFZnCl$ at ∿20°C led to the corresponding substituted trifluorostyrene in 81-83% yield.

It was also possible to react dihalobenzenes with $CF_2{=}CFZnCl$ which made it possible to synthesize trifluorostyrenes containing halogen in the benzene nucleus. On attempting the synthesis of p-halotrifluorostyrenes by reaction of p-chlorophenyl- and p-bromophenyllithium with $CF_2{=}CF_2$ at −80°C only the products of further conversions were obtained, viz. the corresponding symmetrical difluorostilbenes [7]. In reaction with p-chloroiodobenzene, p-chlorotrifluorostyrene was formed in 70% yield after 2 h in THF. Conversion of p-diiodobenzene under analogous conditions gave the same yield however to isolate p-iodotrifluorostyrene failed due to its facile oligomerization.

The reaction with $CF_2{=}CFZnCl$ failed with aryl iodides containing strong electron accepting substituents (NO_2, CN, CO_2Et, CONHMe), only the initial aryl iodides were isolated from the reaction mixture. By analogy with the mechanism proposed in [8, 9] for the combination reaction of other organometallic compounds, it is possible to represent the catalytic reaction of $CF_2{=}CFZnCl$ with ArI as the sequential interaction of $ArPdI(PPh_3)_2$ with $CF_2{=}CFZnCl$ (exchange reaction) leading to the formation of the complex $ArPd(CF{=}CF_2)(PPh_3)_2$ which as a result of reductive elimination of $CF_2{=}CFAr$ was converted into a complex of zerovalent palladium $Pd(PPh_3)_2$. After the oxidation addition of ArI the initial complex $ArPdI(PPh_3)_2$ is regenerated. If seemingly strong electron accepting groups are contained in the aryl then the stable palladium complexes $ArPd(CF{=}CF_2)(PPh_3)_2$ are formed which makes the catalytic reaction impossible. To check this hypothesis the reaction was carried out with a stoichiometric ratio of $CF_2{=}CFZnCl$ and p-$NO_2C_6H_4PdI(PPh_3)_2$ in THF at 20°C. It was established by TLC on Silufol-254 (visualization in UV light) that the initial complex of $R_f = 0.08$ (eluent was hexane: ether = 2:1) almost completely disappeared after 5 min and a new yellow spot with $R_f = 0.15$ appeared. This was visualized, as for all Pd complexes, in iodine vapor and decomposed on heating with the isolation of metallic Pd. There were bands in the IR spectrum of this complex which corresponded to $CF_2{=}CF$ and NO_2 groups.

In addition $CF_2{=}CFSnR_3$ were also used for the alkylation of aryl halides. The cross combination reaction of them iodobenzene catalyzed by palladium complexes $Pd(PPh_3)_4$ and $PhPdI\cdot(PPh_3)_2$ gave the best results. The conversion of the organotin compound reached 80%. Reaction proceeded readily in aprotic dipolar solvents (HMPTA, DMF) at a signfiicant reduction of reaction temperature from 100-120°C in THF to 80°C in HMPTA. It should be recorded that the yield of product after 3 h at 80°C was reduced in the following series of solvents HMPTA—DMF (85-87), DMSO (60), THF (30), C_6H_6 (20), $Cl_2C_6H_4$ (13). However in the case of iodo and nitroso substituted aryl iodides the indicated conditions (HMPTA, 80°C) proved to be drastic and consequently only a mixture of oligomers was formed.

EXPERIMENTAL

Syntheses of organolithium compounds and their conversions were carried out in an atmosphere of dry argon. Trifluorovinyltrimethyltin, complexes of Pd and Ni, and also standard compounds were synthesized by known procedures. Analysis by GLC was carried out on a Tsvet-110 chromatograph with a flame ionization detector in a stream of helium (60 ml/min; column 2 m × 3 mm; sorbent 3% SE-30 on chromaton H super, TLC was on Silufol UV-254 plates, visualization in UV light or iodine vapor.

Trifluorovinylzinc Chloride. A solution of trifluorochloroethylene in a 2:1 mixture of THF—Et_2O was placed at −120°C in a round-bottomed flask fitted with a stirrer, thermometer, and a tube for the introduction of argon. A solution of n-BuLi (15 mmole) in EtO_2 was poured into it. A test for the presence of n-BuLi was negative and the obtained solution was colorless. A solution of anhydrous $ZnCl_2$ (2 g: 15 mmole) in THF (10 ml) was rapidly poured in at the same temperature. The temperature of the mixture was raised at such a rate that there was no blackening. At 0-5°C no solid residue of $ZnCl_2$ remained.

The solution of $CF_2{=}CFZnCl$ in a mixture of THF—EtO_2 obtained in this way was put into the reaction catalyzed by Pd complexes.

Reaction of Trifluorovinylzinc Chloride with Iodobenzene. Iodobenzene (4 g: 20 mmole) in THF (5 ml) and $PhPdI(PPh_3)_2$ (0.167 g: 1%) were added to a solution of $CF_2{=}CFZnCl$ at 5-10°C. The mixture was stirred at 20°C and was observed for the disappearance of iodobenzene by TLC. After 2 h a test sample proved to be negative. The mixture was decomposed with water, acidified with HCl, and extracted with ether. The ether extract was dried with anhydrous Na_2SO_4, the ether was removed, and the residue distilled in vacuum. Trifluorostyrene (1.54 g: 59%) of bp 62-65°C (75 mm) [10] was obtained. The yield was 88%, found by GLC of the reaction mixture.

Reaction of Trifluorovinylzinc Chloride with p-Iodotoluene. A solution of p-iodotoluene (2 g: 10 mmole) in THF (15 ml) and $PhPdIL_2$ (0.16 g: 2%) were added to a solution of $CF_2{=}CFZnCl$ at 10°C, the mixture stirred for 3 h at ∿20°C following the disappearance of p-iodotoluene by TLC. The mixture was decomposed as described above and p-methyltrifluorostyrene (1.4 g: 82%) of bp 90-92°C (70 mm) was obtained $n_D^{20} = 1.4810$ (cf [10]).

Reaction of Trifluorovinylzinc Chloride with p-Iodoanisole. p-Iodoanisole (2.2 g: 9.4 mmole) in THF (10 ml) and $PhPdI(PPh_3)_2$ (0.16 g: 2%) were added to a solution of $CF_2{=}CFZnCl$ at 15°C and the mixture stirred for 2 h at ∿20°C. According to TLC the starting p-iodoanisole was absent. The mixture was decomposed in the usual manner and p-methoxytrifluorostyrene (1.42 g: 81%) was obtained with bp 83°C (10 mm), $n_D^{23} = 1.4925$. Found: C 57.25; H 3.70; F 30.52%. $C_9H_7F_3O$. Calculated: C 57.48; H 3.72; F 30.32%. The structure was confirmed by PMR spectrum.

Reaction of Trifluorovinylzinc Chloride with p-Chloroiodobenzene. p-Chloroiodobenzene (2.5 g: 10 mmole) in THF (15 ml) and $PhPdIL_2$ (0.16 g: 2%) in THF (5 ml) were added to a solution of $CF_2{=}CFZnCl$ (28 mmole) at ∿20°C and the mixture stirred for 2 h until disappearance of p-chloroiodobenzene (by TLC). The mixture was decomposed in the usual manner and after distillation of the solvent the residue was distilled in vacuum. p-Chlorotrifluorostyrene (1.25 g: 66%) was obtained having bp 75-78°C (20 mm), $n_D^{25} = 1.4940$. Found: C 49.62; H 2.28; Cl 18.02; F 29.12%. $C_8H_4ClF_3$. Calculated: C 49.90; H 2.07; Cl 18.41; F 29.60%.

Reaction of Trifluorovinyltributyltin with Iodobenzene. Iodobenzene (0.84 g: 4 mmole), $CF_2\ CFSnBu_3$ (0.67 g: 1.8 mmole), and $PhPdI(PPh_3)_2$ (4.5 mg: 5.4×10^{-5} mole) in THF (5 ml) were placed in an argon atmosphere in a glass ampul. The ampul was evacuated (5.7×10^{-2} mm) sealed, and heated for 9 h at 70°C. The yield of trifluorostyrene was 30% by GLC. This reaction was carried out in a similar manner in C_6H_6 (20%), $(CH_2)_2Cl_2$ (13%), DMSO (20%), DMF (87%), and HMPTA (85%).

Reaction of Trifluorovinyltributyltin with p-Diiodobenzene. p-Diiodobenzene (6.6 g: 20 mmole), $CF_2{=}CFSnBu_3$ (5 g: 40 mmole), and $PhPdI(PPh_3)_2$ (0.48 g: 6×10^{-5} mole) in HMPTA (50 ml) were heated for 6 h at 70°C. After decomposition of the mixture in the usual manner a solid (5.5 g) of mp 180°C (polycondensation product) was isolated.

CONCLUSIONS

A method of obtaining trifluorostyrene and its derivatives (p-Me, p-MeO, p-Cl) has been developed by the cross combination reaction of aryl iodides with trifluorovinylzinc chloride catalyzed by palladium complexes. In the case of aryl iodides with strong electron accepting substitutents a stable palladium complex was formed which did not react in the cross combination reaction. Under more drastic conditions it is possible to use trifluorovinyltrialkylstannanes in place of the organozinc compounds.

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SELENOESTERS IN ORGANIC SYNTHESIS.

1. CONVERSION OF MIXED CARBOXYLIC ACID ESTERS TO SELENOESTERS

A. F. Sviridov, M. S. Ermolenko,
D. V. Yashunskii, and N. K. Kochetkov

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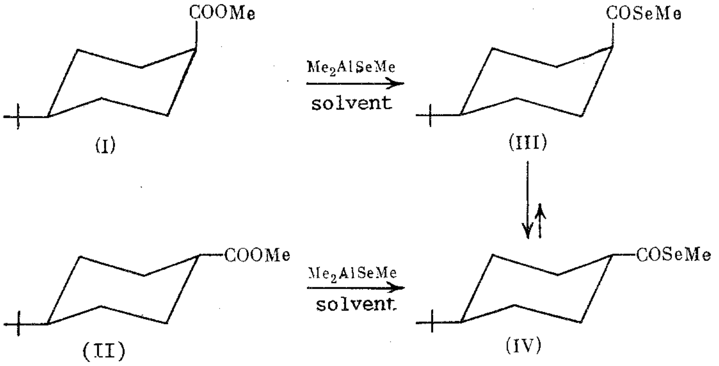
A recurrent problem in organic synthesis involves conversion of mixed esters to ketones of varying structures. One of the better methods of ketone synthesis is based on the reaction of organometallic compounds with carboxylic acid derivatives [1]. The use of mixed esters for this purpose is complicated by difficulties in hydrolyzing the esters and converting the free carboxylic acids to active acylating agents. Although a significant number of methods have been developed recently to deblock or deprotect carboalkoxy groups [2], in many cases (particularly in the synthesis of natural products) this approach is unsuitable due to the lability of the rest of the molecule or to the loss of stereochemistry at a chiral center α to the carboalkoxy group as a result of enolization during the hydrolysis step.

A method was recently reported for the rapid and efficient conversion of mixed esters to selenoesters upon treatment with dimethylaluminum methyl selenide; it was also shown that the latter derivatives easily underwent hydrolysis, alcoholysis, and ammonlysis reactions in the presence of mercury salts [3, 4]. Selenoesters were also found to be more active than their closely related analogs, thioesters. The limits of this reaction, and, more importantly, the effect of steric factors, solvent properties, and other reaction conditions on the course of the reaction, have not been studied.

In order to develop the practical potential of this method in complex organic synthesis, we have investigated the influence of the structure of the starting material, i.e., of the mixed ester, and also the effect of solvent properties on the selectivity of the mixed ester to selenoester conversion reaction. We have also investigated various pathways for the conversion of selenoesters to ketones, particularly α,β-unsaturated ketones, with special attention directed toward the synthesis of complex organic molecules [5, 6].

The esters of cis- (I) and trans-4-tert-butylcyclohexanecarboxylic acid (II) [7] were selected as model compounds in order to assess the behavior of configurationally unstable centers α to the carboalkoxy group under the conditions of selenoester synthesis.



The reaction was conducted in several different solvents (Figs. 1 and 2) in order to determine optimum reaction conditions which would provide a maximum conversion rate and a minimum amount of isomerization of the axial isomer (III) to the equatorial isomer (IV). It

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