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Polymeric reagents

Poly(trifluoroacetoxymercurio)styrene. Preparation and use in reactions with alkyl halides*

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Summary

Poly(styrene-co-divinylbenzene) readily undergoes mercurization with mercuric trifluoroacetate in dichloromethane. The process and extent of mercurization only insignificantly depend on the degree of crosslinking of the polymer containing 1-4 mol.% of the crosslinking agent. By employing this procedure, polymers can be obtained with the mercury content approaching theoretical values. When heated in toluene, mercurized polymers are stable up to 50°C; at higher temperatures they undergo decomposition with splitting of the C-Hg bond. Poly(trifluoroacetoxymercurio)styrene, when reacted with tert-alkyl halides and with alkanes monotopically substituted with the aryl group and bromine, gives the corresponding trifluoroacetates under mild reaction conditions.

Introduction

Solvolytic reactions of alkyltrifluoroacetates proceed at rate constants higher by several orders of magnitude than those of the respective alkylacetates (1). This predetermines the possibility of using them in organic syntheses. Alkyltrifluoroacetates can be prepared by direct esterification of the respective alcohols with trifluoroacetic acid or trifluoroacetanhydride; in some cases the sterically hindered OH group of the alcohol can be resistent to the esterification reaction (2), or the strongly acid medium may become the cause of functional side transformations. A method which is an alternative to direct esterification is the reaction between alkyl halides and silver or mercury(II) trifluoroacetate. The use of $(CF_3COO)_2Hg$ is restricted by the low selectivity of this reagent (in view of the high reactivity of the salt with many functional groups) and by its high toxicity. Even the large amount of findings obtained so far in the research of organomercuric compounds (3,4) did not help to overcome the grave obstacles to their application in chemistry on a major scale, namely, high toxicity, volatility, lipophilic character and the ability to penetrate through cell walls. However, difficulties involved in the application usual organomercuric compounds can be avoided by using polymeric products.

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* To Professor Wichterle on the occasion of his 75th birthday

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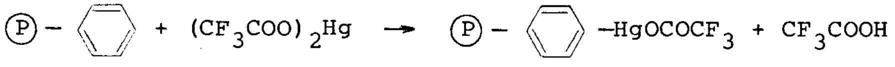
Up to now, polystyrene and other polymers containing aromatic constitutional units have been predominantly mercurized in order to prepare further functional polymer derivatives (5). Only a few authors suggest the potential usefulness of mercurized poly(styrene-co-divinylbenzene) in a direct application as the polymeric reagent (6,7), which makes possible the utilization of general advantages offered by polymeric reagents (8), and also eliminates the danger of intoxication.

Mercury(II), trifluoroacetate is known to be efficient mercurization agent, with which the mercurization of aromatic compounds proceeds at rate constants higher by several orders of magnitude than those with mercury(II) acetate (9). At the same time, acidity of the acid present in the mixture strongly cooperates in this case. The mercurization process of linear and crosslinked polystyrene brought about by mercury(II) trifluoroacetate or mercury(II) acetate is also strongly dependent on the degree of ionization of -O-Hg-O- bonds. Thus, with one equivalent of the Hg^{II} salt used in the mercurization of poly(styrene-co-divinylbenzene) (99:1 mol.%) in THF at 60°C in the case of application of $(CF_3COO)_2Hg$, the degree of mercurization is 34% r.s. (ring substitution; the degree of functionalization, D_f, 0.34), while in the case of $(CH_3COO)_2Hg$ it does not exceed 1% r.s. (5). With respect to the strong dependence of the rate constants of electrophilic mercurization reactions of benzene and toluene on the type of the acid present (10,11), it may be assumed that the mercurization process may be greatly dependent on the type of the aprotic solvent used. So far, the mercurization of polymers containing aromatic constitutional units has been followed only in tetrahydrofuran, nitrobenzene, or 1,4-dioxan (5,12). In this study we report the mercurization of poly(styrene-co-divinylbenzene) with mercury(II) trifluoroacetate at room temperature, the thermal stability of the products and their use as polymeric reagents in the preparation of alkyltrifluoroacetates derived from tert-alkyl alcohols and some aralkyl alcohols.

Results and discussion

Mercurization of the polymer

Mercurization of microporous poly(styrene-co-divinylbenzene) with mercury(II) trifluoroacetate can be described by the scheme:



The reaction took place in dichloromethane at room temperature (23°C). The conversion curves (Fig.1) show that the maximal attainable degree of functionalization, $(D_f)_{theor.}$, defined by the initial molar ratio Hg^{II}/aromatic ring (substitution in one position is assumed), with copolymers having a low content of the crosslinking agent (up to 4 mol.%) is reached virtually after 48 h. This suggests that such experimental procedure is highly efficient. The mercurization of poly(styrene-co-divinylbenzene) (88:12 mol.%) is in all cases much slower, however, obviously due to the fact that neither the starting polymer nor the product swell in the reaction medium, and diffusion of the reactant is a factor which considerably restricts the reaction rate. The content of o, m, p isomers has not been determined, but judging by the results of mercurization of toluene with $(CF_3COO)_2Hg$ in CF_3COOH at 25°C (the ratio of ortho-, meta- and para-isomers of tolylmercury(II) trifluoroacetate is 12.2:8.6: 79.2) (9), substitution in the para-position predominates also in the case of the polymeric analog.

The advantage of the experimental method used consists predominantly in the mild reaction conditions: the initial concentration of $(CF_3COO)_2Hg$ is approximately 10^{-1}mol l^{-1} (corresponds almost to the maximum solubility of the salt in CH_2Cl_2), the reaction proceeds at room temperature. Even under these conditions, however, the reaction rate is higher than the mercurization of polystyrene in tetrahydrofuran or 1,4-dioxan with the solvent at boil (60°C or 101°C), carried out at an almost tenfold concentration of the Hg^{II} salt, and sometimes catalyzed with perchloric acid (5,11). This suggests a favourable effect of dichloromethane used as the reaction medium. This may be explained by assuming that the catalytic effect of the arising trifluoroacetic acid is more strongly operative in CH_2Cl_2 than in THF and 1,4-dioxan. In the case of the catalysis with $HClO_4$ mentioned earlier the evaluation of the mercurization process is moreover complicated by the involved reaction mechanism (5,11), which affects the content of the position isomers and is accompanied by the formation of the Hg^I salt (in the absence of $HClO_4$ no formation of the Hg^I salt was observed (5)).

The reaction of poly(trifluoroacetoxymercurio)styrene[+]

Tert-alkyl bromides and bromoalkanes with a halogen atom and the aryl substituent on the single carbon atom, when reacting with mercurized poly(styrene-co-divinylbenzene) in dichloromethane or chloroform under very mild conditions, readily give very high yields of the respective trifluoroacetates (Table)

I - VI

Analogous chloro derivatives react much more slowly. Primary and secondary alkyl halides do not react at all under similar conditions. Although 2-bromooctane at elevated temperature does react, a mixture of olefins is also formed in this reaction in a low quantity, along with alkyltrifluoroacetate, and the polymeric reagent becomes dark (brown colour); hence, the observed reaction may be a reaction between bromoalkane and the decomposition products of the mercury(II) reagent. It has been observed, namely, that heating of the mercurized polymers above 75°C results in a considerable decrease in weight, which e.g. with poly(styrene-co-divinylbenzene) (98:2 mol.%) mercu-

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[+] A simplified name for the trifluoroacetoxymercurio derivative of poly(styrene-co-divinylbenzene) with substituents on aromatic constituional units.

Table

Reactions between alkyl halides and poly(trifluoroacetoxymercurio)styrene (2 mol.% of crosslinking agent, 25% r.s., 26.5 wt.% Hg, 1.32 mmol Hg/g) to the corresponding alkyltrifluoroacetates (ATFA I-VI). Conversion to ATFA according to GLC (ξ); yields of the isolated products are related to the starting halogen derivative.

Alkyl halide	Solvent	Temperature °C	Time h	ATFA	ξ %	Yield[a] %
Tert.-butyl bromide	CH_2Cl_2	23	0.5	I	98	60
3-Bromo-3-ethylpentane	CH_2Cl_2	23	2	II	98	85
1-Bromoadamantane	CH_2Cl_2	23	0.25	III	100[b]	83
1-Chloroadamantane	CH_2Cl_2	23	4.0	III	21	-
	$CHCl_3$	50	16	III	98	80
2-Bromooctane	$CHCl_3$	50	24	IV	~1	-
	toluene	100	48	IV	13[c]	-
1-Bromo-1-phenylethane	CH_2Cl_2	23	0.25	V	98[b]	82
Benzyl bromide	CH_2Cl_2	23	10	VI	99	81
Benzyl chloride	$CHCl_3$	50	24	VI	11	-

[a] Isolated products show in their IR spectra (cell 0.17 mm, $CHCl_3$ strong absorption values at 1780 cm^{-1} ($-COCF_3$) and 1150 cm^{-1} (C-F). ^1H NMR spectra (CCl_4; δ, ppm): I 1.60 (s,CH_3); II 1.70 (m,6H,CH_2), 1.10 (m,9H,CH_3); III 2.20 (m,9H), 1.70 (m,6H); V 7.26 (m,5H,Ar), 5.90 (q,1H,CH-O), 1.60 (3H,d,CH_3); VI 7.26 (m,5H,Ar), 5.25 (s,2H,CH_2O). [b] After 3 min a 90% conversion of the starting bromo derivative was reached. [c] Along with 2-octyltrifluoroacetate a mixture of 1-octane and 2-octene is formed; the polymer decomposes.

rized to 56% r.s. (38.7 wt.% Hg) can be documented by the following data (% of the starting weight of the polymer/temperature of heating of 0.1 g of the polymer in 1 ml of toluene with stirring for 170 h): 100%/25°C, 99.8%/50°C, 64.0%/75°C, 43.0%/100°C. With decreasing weight the Hg content in the polymer also decreases. This finding must always be born in mind when poly(trifluoroacetoxymercurio)styrene is applied.

The reaction just described is a highly selective method of transformation of tert-alkylbromides and 1-aryl-1-alkylbromides to the respective trifluoroacetates under very mild reaction conditions. Under such conditions, of the other functional groups only the terminal triple bond and some thioacetals can interfere (6). The C-acids and compounds containing C=C double bonds, which are otherwise very sensitive to mercurization reactions, are inert with respect to poly(trifluoroacetoxymercurio)styrene (13).

Experimental part

All solvents were purified by distillation prior to use. Mercury(II) trifluoroacetate (Aldrich) was used without further purification. Poly(styrene-co-divinylbenzene) (United Chemical and Metallurgical Works, Ústí nad Labem, Czechoslovakia), microporous, gel type (beads 200-400 µm), was extracted (Soxhlet) with tetrahydrofuran, and dried (48 h, 40°C, 1.33 Pa) prior to use. 1-Bromoadamantane and 1-chloroadamantane (Aldrich) were used without further purification, the other halogen derivatives were distilled at normal pressure or in vacuo immediately before use.

In the preparation experiments the temperature of the reaction mixture was maintained by means of Term-O-Watch with an accuracy ± 0.5°C. GLC analyses were carried out with a CHROM 5 apparatus (Laboratory Instruments, Prague): column 0.3 x 250 cm, Inerton AW-DMCS (0.125-0.160 µm) + 5% SP 2100, nitrogen as the carrier gas, FID. Microanalysis with respect to mercury was performed complexometrically after the substance had been burnt according to Schöniger. The IR spectra were recorded with a Perkin-Elmer 457 apparatus, the ^{1}H-NMR spectra were recorded with JEOL PS 100.

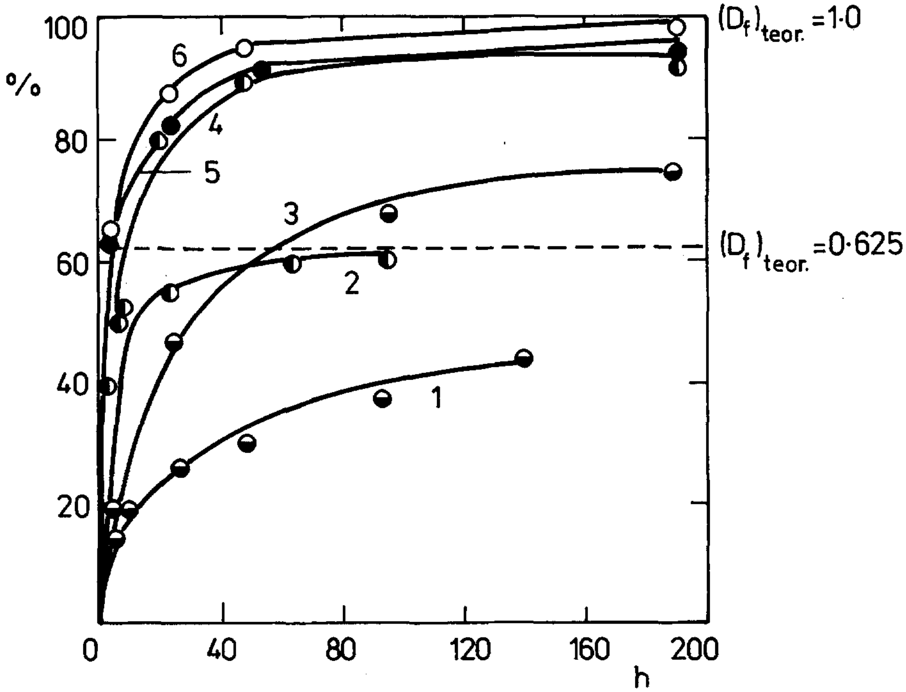

Figure 1, Mercurization of poly(styrene-co-divinylbenzene) by means of $(CF_3COO)_2Hg$ (CH_2Cl_2, 23°C). Content of the cross-linking agent in the copolymer (mol.%): 1, 2, 4, 12. Curves 1 and 2 are related to $(D_f)_{theor.}$ 0.625, curves 3 - 6 are related to $(D_f)_{theor.}$ 1.00.

Mercurization of poly(styrene-co-divinylbenzene) with mercury(II) trifluoroacetate

To 2.500 g of the starting copolymer (content of the crosslinking agent 1,2,4 and 12 mol %; 23.3-24.2 mmoles of aromatic groups), equilibrated with 20 ml CH_2Cl_2, the corresponding volume of a freshly prepared solution of $(CF_3COO)_2Hg$ in CH_2Cl_2 at the concentration 0.10 mol l^{-1} was added with ivigorous stirring (magnetic stirrer). The reaction mixture was slowly stirred without access of air moisture ($CaCl_2$ closure) for the chosen time. After that, the polymer was separated by filtration, washed and extracted (Soxhlet) with dichloromethane, and dried (40°C, 1.33 Pa, 24 h). The degree of functionalization was determined from the Hg content. The IR spectra of all samples (KBr disc) showed the following characteristic absorption values: 820, 860, 1200, 1690 cm^{-1}.

The reaction between alkyl halide and poly(trifluoroacetoxymercurio)styrene

To 2.000 g of the polymeric reagent (2 mol.% of the crosslinking agent, 25% r.s., 2.64 mmol Hg), swollen in 10 ml of solvent (CH_2Cl_2, $CHCl_3$ or toluene), a solution of 2.50 mmoles of alkyl halide in 2 ml of the given solvent was added. The reaction mixture was stirred (magnetic stirrer) and maintained at the reaction temperature for the chosen time. After that, the solution was separated by filtration, the polymer was washed three times with 5 ml of CH_2Cl_2, and the solution was distilled off from the combined fractions. To the raw product (slightly turbid), 5 ml of hexane was added, the solution was filtered, and the solvent was removed by distillation. The product thus isolated was subjected to GLC analysis and characterized by IR and ^1H NMR spectra; it was either chromatographically pure, or contained the starting alkyl halide in an amount corresponding to an incomplete conversion.

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