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THE THIOLATE ANION AS A NUCLEOPHILE

PART IV*. REACTIONS OF SOME PENTAFLUOROPHENYL COMPOUNDS

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SUMMARY

Direct nucleophilic substitution with sodium methanethiolate of the pentafluorophenyl compounds C_6F_5X (X = Cl, Br, I. NO_2, NH_2, CO_2H, SC_6F_5, OMe, OH) has given varying amounts of $XC_6F_4(SMe)$, $XC_6F_3(SMe)_2$, $C_6F_4(SMe)_2$, $XC_6F_2(SMe)_3$ and $C_6F_2(SMe)_4$. In some cases cleavage of the aromatic carbon-X bond (X = Br, I, CO_2H, SC_6F_5) forming $C_6F_4(SMe)H$ and $C_6F_2(SMe)_3H$, and the O-Me bond forming $HOC_6F_2(SMe)_3$ was observed. The new compounds isolated have been characterized by elemental analyses, infrared and mass spectra and their stereochemistries have been deduced from their ^1H and ^{19}F NMR spectra.

INTRODUCTION

This paper is a continuation of a study of the reactions of thiolate anions with fluorine containing aromatic compounds [1]. The reactions of the pentafluorophenyl derivatives C_6F_5X (X = Cl, Br, I, NO_2, NH_2, CO_2H, OMe, and OH) and $(C_6F_5)_2S$ with the methanethiolate anion are described. The results are summarized in the equations shown below, only the major products isolated being shown.

$$C_6F_5Cl + SMe^- \longrightarrow ClC_6F_4(SMe),\ ClC_6F_3(SMe)_2,\ C_6F_4(SMe)_2,\ ClC_6F_2(SMe)_3,\ C_6F_2(SMe)_4$$

$$C_6F_5NO_2 + SMe^- \longrightarrow O_2NC_6F_4(SMe),\ O_2NC_6F_3(SMe)_2,\ O_2NC_6F_2(SMe)_3$$

$$C_6F_5NH_2 + SMe^- \longrightarrow H_2NC_6F_3(SMe)_2$$

$$C_6F_5X + SMe^- \longrightarrow HC_6F_4(SMe),\ HC_6F_2(SMe)_3\text{: X = Br, I, } CO_2H$$

*For Part III, see ref. 1.

$C_6F_5OMe + SMe^- \longrightarrow MeOC_6F_4SMe,\ HOC_6F_2(SMe)_3$

$(C_6F_5)_2S + SMe^- \longrightarrow [C_6F_4(SMe)]_2S,\ [C_6F_2(SMe)_3]_2S,\ HC_6F_2(SMe)_3$

RESULTS AND DISCUSSION

The reactions were studied in the same solvent as used in the previous parts of this series, namely a mixture of ethylene glycol-pyridine, volume ratio approximately 1:2. In the reactions described at least two fluorine atoms always remained on the aromatic ring. This has been observed previously using the same solvent mixture [1,2]. However if other solvents were employed complete replacement of the fluorine may occur; for example, the fluorine atom in fluorobenzene was replaced by the SBu group using HMPA/THF as solvent [3].

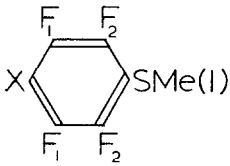
The relative influence of the group X on the reactivity of the C_6F_5 group towards nucleophilic substitution can be estimated from the reaction temperature and time. The most reactive substrate was $C_6F_5NO_2$ and the solution needed cooling. An approximate reaction rate series can be deduced for C_6F_5X when $X = NO_2 > SC_6F_5 >$ F,H,Cl, Br, I, NH_2, $CO_2H >$ OH, OMe.

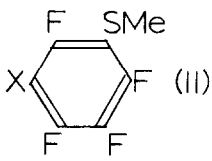
The replacement of a Br, I, or CO_2H by H during the course of nucleophilic substitution is not unusual. A radical mechanism has been postulated for the replacement of bromine or iodine by hydrogen during nucleophilic substitution [4,5]. Similarly a mixture of tetrabromobenzenes resulted from the reaction of hexabromobenzene with sodium methoxide [6]. Cleavage of the Me-O bond in C_6F_5OMe when treated with various nucleophiles has also been observed [7]. Previous results on the nucleophilic substitution of pentafluorobenzoic acid in refluxing methanol enabled 2,3,5,6-tetrafluoro-4-(methylthio)benzoic acid to be isolated. Some decarboxylation occurred, however, when the nitrogen nucleophiles $MeNH_2$ and Me_2NH were used [8]. The temperature of the refluxing pyridine/ethylene glycol mixture was higher than that of refluxing methanol and may account for the decarboxylation observed. In the reaction of pentafluorophenol with the methanethiolate anion a product containing no sulfur was isolated. The compound *p*-$MeSC_6F_4OH$ was prepared from pentafluorothioanisole, C_6F_5SMe, and the hydroxide ion acting as a nucleophile.

$C_6F_5SMe + OH^- \longrightarrow$ *p*-$HOC_6F_4SMe + F^-$

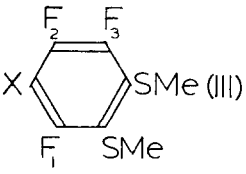
The position of initial replacement depends on the group X initially present in C_6F_5X [9]. In most cases the activating influence of the fluorine with respect to the point of nucleophilic attack is predominant, and is in the order *meta* > *ortho* > *para*. However, when the group X is a very effective elec-

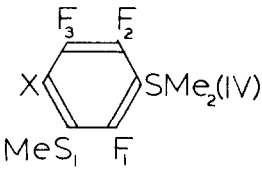
tron pair donor, such as NH_2 or OMe, then electron pair repulsion predominates and substitution occurs mainly meta to the group X [9]. The structures I and II for the monosubstituted compounds should predominate, the actual product depending on the nature of X. Only compounds of structure I were isolated, but

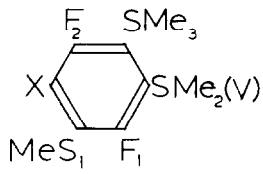




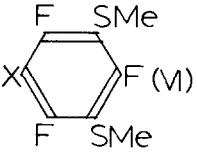
no monosubstituted product was isolated using pentafluoroaniline, where product II might be expected. Further nucleophilic substitution of I should give III or IV and then V. Further nucleophilic substitution of II might be

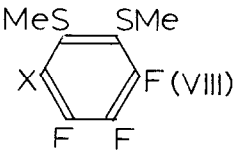






expected to give VI, or possibly III, VII, or VIII.

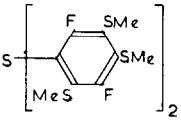




The stereochemistries of the products have been deduced from their ^1H and ^{19}F NMR spectra, details of which are shown in Table 1, together with the spectra of some analogous compounds. The methyl hydrogen-ortho fluorine coupling constants have been deduced from both the proton and fluorine spectra and were approximately 1 Hz, consistant with previous observations [10]. Two separate mechanisms can be postulated.

$C_6F_5X \longrightarrow I \longrightarrow IV \longrightarrow V$ (X = Cl, NO_2, OMe)

$(C_6F_5)_2S \longrightarrow IX \longrightarrow X$ IX = $(p\text{-}MeSC_6F_4)_2S$, X =



$C_6F_5X \longrightarrow$ (II) $\longrightarrow$ VII $\longrightarrow$ V (X = Cl, NH_2)

Products of structure II might be expected when X = OMe or NH_2, but when X = OMe product I was formed and no monosubstituted product was isolated when X = NH_2. The nature of the group X has, therefore, little effect on the position of substitution.

TABLE 1

Summary of NMR spectral data

COMPOUND	Chemical Shifts§		Coupling Constants/Hz				
	^{1}H/p.p.m.	^{19}F/p.p.m.	J(H-F)	J(H-F)(H)	J(F-F_o)	J(F-F_m)	J(F-F_p)
I, X = Cl	2.59 T	146.6(1)	1.0	---	---	---	---
		134.3(2)	---	1.0	---	---	---
I, X = NO_2	2.77 T	148.1(1)	1.6	---	---	---	---
		133.3(2)	---	1.6	---	---	---
I, X = OMe	4.09(OMe)T	156.9(1)	1.45	1.5	22.8	3.0	8.4
	2.44 T	135.2(2)	< 0.5	0.6	22.8	0.9	8.4
I, X = OH	2.47 T	161.8(1)	0.4	---	23.7	2.7	8.5
	6.08(OH)S	134.7(2)	---	0.45	23.5	2.7	8.5
IX	2.57 T	132.5(1,2)	1.01	---	---	---	---
I, X = H (ref.1)	2.54 T	---	0.95	---	---	---	---
VII, X = Cl	2.60(1)D	108.5(1)	1.75	0.9	---	2.65	12.6
	2.57(2)T	130.3(2)	0.9	0.9	25.3	2.65	---
	---	132.9(3)	---	1.85	25.4	---	12.8
IV, X - NO_2	2.55(1)D	100.1(1)	0.8	1.3,0.7	---	5.3	13.2
	2.68(2)T	126.8(2)	1.3	1.4	24.3	5.3	---
		149.8(3)	---	---	24.2	---	13.2
VII, X = NH_2	2.37(1)+	132.8(1)	---	1.0	---	5.0	13.0

+ Half peak width ca. 0.9 Hz *too complicated §TMS and $FCCl_3$ as internal standards

COMPOUND	Chemical Shifts§		Coupling Constants/Hz				
	^{1}H/p.p.m.	^{19}F/p.p.m.	J(H-F) (F)	J(H-F)(H)	J(F-F_o)	J(F-F_m)	J(F-F_p)
	2.52(2)T	146.2(2)	0.96	1.0	25.5	5.0	---
	4.42(NH_2)S	135.7(3)	---	(0.6)	24.5	---	13.0
V, X = Cl	2.52 D	99.4(1)	1.55	1.5,1.5	---	---	14.8
	2.54 D	107.6(2)	1.55	2.3	---	---	14.9
	2.57(3)D	---	2.15	---	---	---	---
V, X = NO_2	2.52(1)D	100.3(1)	1.0	1.0,2.65	---	---	15.5
	2.60(2)D	122.0(2)	2.65	2.65	---	---	15.5
	2.60(3)D	---	2.65	---	---	---	---
V, X = OH	2.34(3)D	100.4(1)	0.8	0.7	---	---	14.6
	2.35(1)S	129.9(2)	---	2.5	---	---	14.5
	2.60(2)D	---	2.6	---	---	---	---
	6.64(OH)S	---	---	---	---	---	---
X	2.395(2)D	101.0(1)	1.97	*	---	---	14.63
	2.479(1)D	100.9(2)	1.21	*	---	---	14.63
	2.519(3)D	---	1.99	---	---	---	---
$[(MeS)_3C_6F_2]_2$ (ref.2)	2.305(1)D	101.69(1)	1.0	---	---	---	14.2
	2.515(2)D	106.61(2)	1.8	---	---	---	16.9
	2.602(3)D	---	2.0	---	---	---	---
V, X = H (ref.1)	2.520(1)S	110.00(2)	1.43	1.39	---	---	15.25
	2.583 D	109.08(1)	1.96	2.05	---	---	---
	2.641 D	---	---	---	---	---	---

*too complicated

§ TMS and $FCCl_3$ as internal standards

As the products VII as well as I (X = Cl) were isolated from the reaction of C_6F_5Cl, the reactions of I (X = Cl) and VII (X = Cl) with SMe^- were studied further, particularly to observe whether I (X = Cl) could be converted to VII (X = Cl) or directly to V (X = Cl) and whether VII (X = Cl) could be converted to V (X = Cl). The results are shown in the equations

$$C_6F_4Cl(SMe)\ (I) + SMe^- \longrightarrow \underline{p}\text{-}(MeS)_2C_6F_4\ (4\%) + C_6F_3Cl(SMe)_2\ (4\%) + C_6F_2Cl(SMe)_3(V)\ (45\%)$$

$$C_6F_3Cl(SMe)_2(VII) + SMe^- \longrightarrow \underline{p}\text{-}F_2C_6(SMe)_4\ (60\%) + C_6F_2(SMe)_3(V)\ (20\%)$$

and indicate that both the F and Cl atoms in the compounds are somewhat labile towards SMe^- as a nucleophile. It was not possible to separate the approximately 1:1 mixture of $\underline{p}\text{-}(MeS)_2C_6F_4$ and $C_6F_3Cl(SMe)_2$ by conventional chemical means, such as TLC, column chromatography, sublimation, or recrystallization. The mass spectrum indicated the presence of both products, as did the ^1H and ^{19}F NMR spectra which were poorly resolved. In CCl_4 solution the signals corresponding to $\underline{p}\text{-}(MeS)_2C_6F_4$ were observed as singlets at 133.69 p.p.m. (F, $FCCl_3$ ext. std.) and 2.498 p.p.m. (H, TMS, int. std.) (lit. values, $CDCl_3$ solvent, 134.67 and 2.505 p.p.m. respectively [2]). Other signals were observed at 107.00 p.p.m. doublet, (J(F-F) 12.0 Hz), 128.59 p.p.m. doublet, (J(F-F) 24.0 Hz), and 131.11 p.p.m. doublet of doublets, (J(F-F) 12.00, 24.00 Hz) in the F spectra (all peaks half peak width ca. 4 Hz) and possible superimposed triplet (J(H-F) 0.9 Hz) and doublet (J(H-F) 2.2 Hz) at 2.49 p.p.m. in the proton NMR. These results indicate that the other component may be VII (X = Cl) (see later), which may have been formed either by rearrangement or due to a trace of, for example, II (X = Cl) in the starting material I (X = Cl).

The monosubstituted products I and II should have entirely different fluorine NMR spectra. The fluorine spectra of all the monosubstituted products showed two distinct but equal signals. The fluorine with chemical shift around 134 p.p.m. can be assigned as that ortho to the SMe group, and this was confirmed by the observed splitting into a quartet due to coupling to the three protons in the methyl group. The chemical shift of the fluorine atoms ortho to the SMe group in $\underline{p}\text{-}(MeS)_2C_6F_4$ and $MeSC_6F_5$ are 134.7 and 134.2 p.p.m. respectively [2,12]. Similarly in $(C_6F_5)_2S$ the chemical shift of the fluorine atoms ortho to the sulfur is 132.4 p.p.m. [12]. It was therefore not surprising that in $(\underline{p}\text{-}MeSC_6F_4)_2S$ two distinct fluorine signals could not be detected as all the fluorine atoms are ortho to one fluorine and one sulfur. The fluorine spectra observed in $\underline{p}\text{-}XC_6F_4Y$ were not first order, and could be assigned as A_2B_2 [13], but may be more complex as in the case of $\underline{p}\text{-}MeSC_6F_4NO_2$ where an $AA'MM'X_3$ system with partial $AA'BB'X_3$ character was found. The flu-

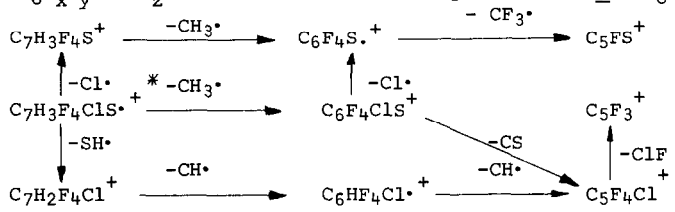
orine atoms meta to the SMe group are not coupled to the methyl protons and were used to calculate the coupling constants, assuming an A_2B_2 spectrum. The coupling constants deduced are within the range found in the compounds p-XC_6F_4Y [13,14].

The fluorine spectra of the disubstituted products $(MeS)_2C_6F_3X$ (X = Cl, NO_2, NH_2) all showed that three distinct fluorine atoms were present. The spectra were first order and the fluorine-fluorine coupling constants deduced showed that the fluorine atoms were ortho, meta, and para to each other, as in structures III,IV, and VII. Some of the fluorine signals were further split into quartets or quartets of quartets by coupling to the protons of one or two ortho methyl groups respectively. The spectra were consistent with the structure IV when X = NO_2, as one of the fluorine signals (F_3) was not split by coupling to a methyl group, one (F_2) was split into a quartet, and one (F_1) into a quartet of quartets. The structure VII was consistent with the fluorine spectra when X = Cl or NH_2. Each of the fluorines was split into a quartet by coupling to the protons of an ortho methyl group. No evidence was found for structure III.

The structure V is the only one consistant with the observed fluorine and proton NMR spectra of the compounds $(MeS)_3C_6F_2X$. The fluorine-fluorine coupling constants were about 15 Hz indicating para fluorine atoms [14]. The signal around 100 p.p.m. can be assigned to F_1 due to its similarity to that observed in p-$F_2C_6(SMe)_4$ at 99.95 p.p.m. [15]. The fluorine and methyl proton peaks were further split by fluorine-methyl proton coupling.

Although the infrared spectra cannot be used for the absolute determinations of the structure they did enable the presence of groups such as OH and NH_2 to be detected. As the degree of substitution of the aromatic nucleus with SMe groups increased the C-H stretching frequency was observed to change,being 3000 cm^{-1} for the mono-substituted derivatives, 3010 cm^{-1} for the disubstituted derivatives, and 3020 cm^{-1} for the trisubstituted derivatives.

The mass spectra of all the products have been examined and all confirm the mono-isotopic molecular weights. The fragmentation patterns and spectra are very similar to those observed previously for the fluorobenzene derivatives $C_6F_xH_y(SMe)_z$ [1]. The initial decomposition of p-ClC_6F_4SMe is shown below.



The spectra below m/e about 120 are all very similar and analogous to those observed for the pentafluorophenylthio derivatives C_6F_5SX [16]. This indicated that fragmentation gave primarily residues containing only carbon, fluorine and sulfur. The methyl groups, some of the sulfur, and the other group X present in the original compound $XC_6F_x(SMe)_y$ must have been fractured relatively readily from the molecular ion, or its immediate decomposition products.

EXPERIMENTAL

All the pentafluorphenyl compounds were available commercially. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, West Germany. The analytical data and some physical properties of the new compounds are shown in Table 2. Infrared spectra were recorded on a Perkin-Elmer model 457 spectrophotometer as thin films, as mulls with Nujol of hexachlorobutadiene. or as KBr discs. Mass spectra were recorded on a DuPont/CEC Model 21-110B mass spectrometer using indirect introduction techniques. NMR spectra were recorded in CCl_4 solution using TMS or $FCCl_3$ as internal standards on a Varian HA 56/60 or XL 100, or Bruker HX 60.

TABLE 2

Chemical analyses and physical properties of new compounds

Compounds	M.p./°C or b.p./°C/Torr	Color	Calculated (%)			Found (%)		
			C	H	S	C	H	S
$C_6F_2(SMe)_3Cl$	48.5-50.5	white	37.8	3.1	33.5	37.9	3.1	33.4
$C_6F_4(SMe)Cl$	62-64/o.3	none	36.5	1.3	13.9	36.6	1.4	13.9
$C_6F_3(SMe)_2Cl$	63-64	white	37.1	3.2	24.8	37.3	2.3	24.9
$C_6F_2(SMe)_3NO_2$	52-54	yellow	36.4	3.1	32.4	36.7	3.1	32.7
$C_6F_3(SMe)_2NO_2$	102-4/o.3	yellow	35.7	2.3	23.8	36.2	1.3	23.4
$C_6F_4(SMe)NO_2$	64-66/o.3	yellow	34.9	1.3	13.3	34.7	1.4	13.2
$C_6F_3(SMe)_2NH_2$	53-54	white	40.2	3.4	26.8	40.1	3.4	26.9
$C_6F_4(SMe)(OMe)$	58-60/o.2*	none	42.5	2.7	14.2	42.6	2.7	14.0
$[C_6F_2(SMe)_3]_2S$	79-80	white	40.4	3.4	42.0	40.5	3.3	41.4
$[C_6F_4(SMe)]_2S$	69.5-70	white	39.8	1.4	22.8	39.8	1.6	23.1
$C_6F_4(SMe)_3OH$	72.5-73	white	40.3	3.7	35.8	40.2	3.8	35.9
$C_6F_4(SMe)OH$	60-69	white	39.6	1.9	15.1	39.6	2.0	14.8

*lit. value b.p. 118°mm. Hg[17].

The procedure followed in the preparative work has been described previously [2]. Under normal conditions the thiol, dissolved in NaOH/ethylene glycol, was added slowly to the C_6F_5X in refluxing pyridine. The final ratio pyridine:ethylene glycol was 2:1. Refluxing was continued for a further 15 mins. before quenching by pouring onto crushed ice acidified with conc. HCl (final ratio water: HCl, approximately 4:1). Any precipitate was filtered off and the product extracted with ether. In some cases this procedure had to be modified somewhat. The reaction with $C_6F_5NO_2$ was studied completely at 0°C. Using $(C_6F_5)_2S$ the reaction mixture was only refluxed for 15 min. after addition of the nucleophile and then stirred for 10 min. before quenching. With the substrates C_6F_5OMe and C_6F_5OH the pyridine solution was refluxed for 20 min. before addition of the nucleophile and then refluxed for 15 min. after the addition. It was further stirred for 20 min. before quenching.

The products were isolated by distillation in vacuo, recrystallization, sublimation, column chromatography, either singly or in combination. Chromatography was effected on 50 g silica gel, 40-140 mesh, with hexane-ether gradient elution.

Details of the experimental conditions are shown in Table 3. The known products $C_6F_4(SMe)_2$[2], $C_6F_2(SMe)_4$[2], $C_6F_4(SMe)H$[1] and $C_6F_2(SMe)_3H$[1] were characterized by their m.p.'s, IR and NMR spectra. $(MeS)C_6F_4(OMe)$ has been prepared from $MeSC_6F_5$ and OMe^-[17]. In the reaction with C_6F_5OH an unidentified colorless liquid product, b.p. 24-6°/0.3 Torr was isolated (Found: C, 40.1; H, 2.10; S 0.2%). The proton NMR of this product showed the presence of an OH group and a C_2H_5 group, approximate ratio 1:2. The fluorine NMR was not as clear and could not be interpreted. The reaction of $MeSC_6F_5$ with the OH^- nucleophile in conditions similar to those above but omitting the thiol, yielded p-$MeSC_6F_4OH$.

ACKNOWLEDGEMENTS

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TABLE 3

Reaction stoichiometry and products

Substrate	Molar ratio MeS^-:substrate	Major product	Yield (%)	Purification
C_6F_5Cl	4	$C_6F_2(SMe)_3Cl$	70	2(MeOH),3
C_6F_5Cl	1	$C_6F_4(SMe)Cl$	47	4,1
		$C_6F_3(SMe)_2Cl$	32	4,3
C_6F_5Br	4	$C_6F_2(SMe)_3H$	40	3
C_6F_5Br	1	$C_6F_4(SMe)H$	15	1
C_6F_5I	4	$C_6F_3(SMe)_3H$	57	2(MeOH),3
C_6F_5I	1	$C_6F_3(SMe)_3H$	17	2(MeOH)
$C_6F_5NO_2$	4	$C_6F_2(SMe)_3NO_2$	22	2(MeOH),3
		$C_6F_3(SMe)_2NO_2$	10	4,1
		$C_6F_4(SMe)NO_2$	10	4,1
$C_6F_5NO_2$	1	$C_6F_4(SMe)NO_2$	42	1
		$C_6F_3(SMe)_2NO_2$	23	1
$C_6F_5NH_2$	4	$C_6F_3(SMe)_2NH_2$	49	3
$C_6F_5NH_2$	1	$C_6F_3(SMe)_2NH_2$	34	3
$C_6F_5CO_2H$	4	$C_6F_2(SMe)_3H$	80	2(MeOH)
$C_6F_5CO_2H$	1	$C_6F_4(SMe)H$	60	1
	C	$C_6F_2(SMe)_3H$	13	2(MeOH)
$(C_6F_5)_2S$	8	$[(MeS)_3C_6F_2]_2S$	10	4,2(i-BuOH)
		$C_6F_2(SMe)_3H$	28	4,3
$(C_6F_5)_2S$	2	$[(MeS)C_6F_4]_2S$	64	4,3
C_6F_5OMe	4	$C_6F_2(SMe)_3OH$	74	4,3
C_6F_5OMe	1	$(MeS)C_6F_4(OMe)$	44	1
$C_6F_4Cl(SMe)$	1	$C_6F_3Cl(SMe)_2$	4	4,3
		$C_6F_4(SMe)_2$	4	4,3
		$C_6F_2Cl(SMe)_3$	45	4,3
$C_6F_3Cl(SMe)_2$	1	$C_6F_2Cl(SMe)_3$	20	4,3
		$C_6F_2(SMe)_4$	60	4,3

Purification: 1=distillation in vacuo, 2=recrystallization, 3=sublimation, 4=column chromatography.

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