FLUOROALIPHATIC DERIVATIVES OF MERCURY

COMMUNICATION 2. DEMERCURATION OF 2-CHLOROMERCURI-3,3,3-TRIFLUORO-1-PROPANOL AND ITS ETHERS

V. R. Polishchuk, L. S. German,
and I. L. Knunyants

UDC 542.91 + 547.254.9 + 547.263 + 546.16

Hydroxymercuration and subsequent reduction is used for the indirect hydration of olefins, the direct hydration of which is difficult [1]. 3,3,3-Trifluoropropene enters with difficulty into the polar addition reaction. Hydrogen chloride and hydrogen bromide add to it only at 100° in the presence of aluminum halides. It does not react with water in acid medium, while conc. H_2SO_4 mineralizes the fluorine atoms. Nucleophilic reagents do not add to 3,3,3-trifluoropropene. Also primary amines, sodium methylate and acetic acid in weakly basic medium do not react with it. The action of water and alcohols, in the presence of bases, under drastic conditions, leads to mineralization of the fluorine atoms [2, 3]. The mercuration of 3,3,3-trifluoropropene with mercuric nitrate in glacial acetic acid or in absolute alcohol proceeds with great ease, leading (after treatment with KCl solution) to the crystalline ethers of 2-chloromercuri-3,3,3-trifluoro-1-propanol [4].

$$\underset{(R\text{—alkyl, acetyl})}{CF_3CH{=}CH_2 \xrightarrow[ROH]{1)\ Hg(NO_3)_2;\ 2)\ KCl}} \underset{(I)}{CF_3CH(HgCl)CH_2OR}$$

In order to develop a convenient synthesis for 3,3,3-trifluoro-1-propanol and its ethers and esters, we studied the reaction of the (I) compounds with reducing agents.

It is known that mercury in organic compounds is replaced by hydrogen when the organic compounds are treated with sodium borohydride [1], zinc dust [5] or hydrazine hydrate, in which connection the last reaction is accomplished via the step of symmetrization of the organomercury compound [6]. When bis-(polyfluoroalkyl) derivatives of mercury, (R_2Hg), are treated with moist Al the mercury is replaced by hydrogen, if $R = CF_3$, C_2F_5, C_3F_7 or $CHFCF_3$, while vinylidene fluoride [7] is formed when $R = CH_2CF_3$.

We established that the (I) compounds, when reduced in aqueous suspension with an alkaline solution of sodium borohydride, form the corresponding 3,3,3-trifluoro-1-propanol derivatives in 50-80% yield.

$$\underset{(I)}{CF_3CH(HgCl)CH_2OR} \xrightarrow[KOH]{NaBH_4} \underset{(II)}{CF_3CH_2CH_2OR} \ (R{=}H,\ CH_3,\ COCH_3)$$

When $R = COCH_3$, the ester function is retained due to the use of KOH in an amount equivalent to the amount of organomercury compound. 3,3-Difluoroallyl alcohol and its ethers are formed in good yield (50-89%) when an attempt is made to reduce the (I) compounds with zinc dust in saturated NH_4Cl solution.

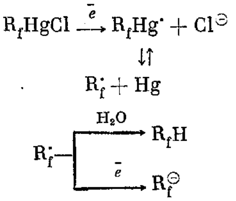
$$\underset{(I)}{CF_3CH(HgCl)CH_2OR} \xrightarrow[NH_4Cl]{Zn} \underset{(III)}{CF_2{=}CHCH_2OR} \ (R{=}H,\ \text{alkyl})$$

The side desoxymercuration reaction leads to the formation of 3,3,3-trifluoropropene. When $R = COCH_3$, the desoxymercuration reaction predominates. The formation of the (III) compounds is an example

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 798-802, April, 1971. Original article submitted July 9, 1969.

of the cleavage of mercury and of the fluorine atom adjacent to it from the organic molecule. Fluorine in the β-position to the mercury atom differs in its properties from other halogens. Organofluorine derivatives of mercury are not inclined to undergo reactions involving the β-elimination of fluorine. Thus, according to the literature data, the (I) compounds during pyrolytic decomposition do not cleave the elements of HgFCl, but instead liberate 3,3,3-trifluoropropene [4]. The bisperfluoroalkyl compounds of mercury during pyrolysis do not liberate the olefin, but instead metallic mercury and the recombination product of the organofluoro radicals [8].

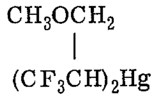
As a result, organofluoroderivatives of mercury are normally reduced by a metal, provided they contain fluorine in the α-position to the mercury [7], and they eliminate fluorine from the β-position when the α-fluorine is absent. Starting with the polarography data [9], these transformations can evidently be depicted by the following scheme:



The electron, supplied by the metal atom, causes the elimination of chlorine as the anion. Knowing that an α-fluorine stabilizes radicals and in part destabilizes carbanions [10], it may be assumed that $R_f^\cdot$ reacts with water when an α-fluorine is present. When an α-fluorine is absent the radical obtains a second electron and is converted to the carbanion.

$$CF_3CH{=}CH_2 \xleftarrow{-RO^\ominus} CF_3\overset{\ominus}{C}HCH_2OR \xrightarrow{-F^\ominus} CF_2{=}CHCH_2OR$$

In the case of the (I) compounds studied by us the stabilization of the carbanion can occur along two competing directions: cleavage of either a fluorine anion or $RO^\ominus$. The first path predominates when R = H or alkyl, while the second path predominates when R = $COCH_3$.

Reduction of the (I) compound (R = CH_3) with hydrazine hydrate in ethylene glycol at 130° leads to the formation, in low yield, of a mixture of the (II) and (III) compounds (R = CH_3), while at 100°, without a solvent, only the symmetrization product of the starting compound  $(CF_3\underset{|}{\overset{CH_3OCH_2}{C}}H)_2Hg$ (V) is formed.

It can be seen that at elevated temperature, together with normal reduction via the symmetrization step, there occurs a radical reaction according to the above-given scheme.

EXPERIMENTAL

The hydroxymercuration of 3,3,3-trifluoropropene was run as decribed in [4].

Reaction of (I) Compounds with $NaBH_4$. To a stirred suspension of 0.033 mole of (I) in 15 ml of water was slowly added in drops a solution of 0.6 g of $NaBH_4$ in 10 ml of water, containing 1.9 g of KOH. Mercury is liberated in 87-99% yield. See below for the isolation of the liquid products and their properties.

Reaction of (I) Compounds with Zinc Dust. To a mixture of 0.033 mole of (I), 13 g of Zn dust and 15 g of NH_4Cl was rapidly added 40 ml of water. Reaction began immediately with the evolution of gas, which was collected and analyzed by GLC.* When R = H or alkyl, the yield of 3,3,3-trifluoropropene was 6-10%; when R = $COCH_3$, the yield was 74%. Compound (III) (R = H) is quantitatively converted to $CF_2BrCHBrCH_2 \cdot OH$ (IV) by bromination in anhydrous $CHCl_3$. See below for the isolation and properties of the liquid products.

Reaction of (I) Compounds (R = CH_3) with Hydrazine Hydrate. A mixture of 0.1 mole of (I) (R = CH_3) and 0.4 mole of hydrazine hydrate in 150 ml of ethylene glycol, containing added cetyl alcohol, was slowly heated up to 130°. The liquid that distilled off contains a 50-51° fraction, which, based on the GLC data, is composed of compounds (II) and (III) (R = CH_3) in a 1 : 1 ratio. The yield of Hg was 83.5%.

---

*All of the analyses of the liquids and gases by GLC were run on Porapak Q sorbent at 170-175°.

TABLE 1. Properties of Synthesized Compounds

Compound	Yield, %	Bp, °C (p, mm of Hg) or Mp, °C	n_D^{20}	Found, %			Calculated, %			Characteristic band in IR spectrum, cm^{-1}
				F	C	H	F	C	H	
(I) $R{=}CH_3$	70	62—63	—	15,46 15,28	13,22 13,08	1,80 1,88	15,69	13,23	1,67	
(I) $R{=}i\text{-}C_3H_7$	54	34—35	—	14,50 14.60	18,32 18.45	2,36 2,43	14,57	18,42	2,58	
(II) $R{=}H$	50,7	98—102 *	—	Identical with authentic samples when based on GLC data						
(II) $R{=}CH_3$	80	53—54 †	1,3120							
(II) $R{=}COCH_3$	61	112—113 ‡	1,3432	36,18 36,29			36,51			
(III) $R{=}H$	50	40—41(20)	1,3605	40,01 39,65			40,38			1742
(III) $R{=}CH_3$	66	45—46	1,3386	35,22 34,93			35,15			1726
(III) $R{=}C_2H_5$	65	63—64 **	1,3540							1757
(III) $R{=}i\text{-}C_3H_7$	89,4	81	1,3640		52,78 52,61	7,96 7,91		52,92	7,42	1762
(IV)	98	69—70(10)	1,4808	14,44 14,44	14,73 14,66	1,84 1,77	14,97	14,19	1,59	
(V)	42,3	86—87(10)	1,4176	24,43 24,17	22,05 21,94	2,78 2,87	25,04	21,13	2,66	

---

* From [11]: bp 100-101°.

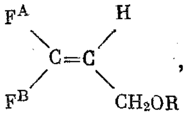
† From [12]: bp 54.9°; n_D^{20} 1.3114.

‡ From [13]: bp 112°; n_D^{20} 1.3428.

** From [14]: bp 67° (760 mm); n_D^{20} 1.3548.

A mixture of 0.05 mole of (I) ($R = CH_3$) and 15 ml of hydrazine hydrate was heated on the boiling water bath for 2 h. The liberation of volatile substances was not observed. The amount of obtained Hg was 0.026 atom.

Isolation of Liquid Products. The low-boiling liquids were isolated by direct distillation from the reaction mixture; the liquids, boiling above 85°, were extracted with ether, the extracts were dried over $MgSO_4$, and the ether was distilled off through a fractionating column. The residues were distilled.

NMR Spectra of Synthesized Compounds. All of the F^{19} NMR spectra were recorded on a Hitachi H-60 instrument. The chemical shifts were measured relative to CF_3COOH as the external standard. The H^1 NMR spectra were recorded on a Perkin–Elmer R-12 instrument, using hexamethyldisiloxane as the internal standard. The values of the proton chemical shifts are given on the δ scale. Compound (I), F^{19} (in $CHCl_3$): $\delta_{CF_3} = -21\text{-}21.6$ ppm, $J_{F^{19}-H} \approx 13$ Hz, $J_{F^{19}-Hg^{199}} \approx 315$ Hz. Compound (V), F^{19}: $\delta_{CF_3} = -21.4$ ppm, $J_{F^{19}-H^1} = 12.3$ Hz, $J_{F^{19}-Hg^{199}} = 256$ Hz. Compound (III) , F^{19}: system ABX, $\delta_{CF_2} = +11.4\text{-}12.2$ ppm, $J_{F^A-F^B} \approx 40.4$ Hz, $J_{F^A-H} = 2.5$ Hz, $J_{F^B-H} = 22.6\text{-}24.1$ Hz. $CF_3\overset{III}{CH_2}\overset{II}{CH_2}\overset{I}{OH}$, NMR: $\delta_I = 4.74$, $\delta_{II} = 3.72$; $\delta_{III} = 2.21$ ppm, $J_{H^{II}-H^{III}} = 6$ Hz, $J_{H^{III}-F^{19}} = 11$ Hz.

The properties of the synthesized compounds are given in Table 1.

CONCLUSIONS

1. A preparative method was developed for the synthesis of 3,3,3-trifluoro-1-propanol and its ethers and esters from 3,3,3-trifluoropropene.

2. It was shown that the β-elimination of fluorine occurs when 2-chloromercuri-3,3,3-trifluoro-1-propanol and its ethers are treated with zinc, leading to the formation of 3,3-difluoroallyl compounds.

LITERATURE CITED

1. H. C. Brown and P. Geoghegan, J. Amer. Chem. Soc., 89, 1522 (1967).
2. A. L. Henne and S. Kaye, J. Amer. Chem. Soc., 72, 3369 (1950).
3. A. L. Henne, J. V. Schmitz, and W. G. Finnegan, J. Amer. Chem. Soc., 72, 4195 (1950).

4. I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 88 (1961).
5. K. Ichikawa, S. Fukushima, H. Ouchi, and M. Tsuchida, J. Amer. Chem. Soc., 80, 6005 (1958).
6. G. F. Wright, Can. J. Chem., 30, 268 (1952).
7. A. N. Stear and J. J. Lagowski, J. Chem. Soc., Suppl. No. 1, 5848 (1964).
8. P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, J. Org. Chem., 28, 184 (1963).
9. R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, J. Amer. Chem. Soc., 88, 460 (1966).
10. I. L. Knunyants, L. S. German, and I. N. Rozhkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1062 (1966).
11. R. N. Haszeldine, J. Chem. Soc., 1273 (1954).
12. A. L. Henne and M. Smook, J. Amer. Chem. Soc., 72, 4378 (1950).
13. L. S. German and I. L. Knunyants, Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva, 11, 356 (1966).
14. P. Tarrant and E. C. Stump, J. Org. Chem., 29, 1198 (1964).