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FACILE H-D EXCHANGE OF METHYL HYDROGENS OF $(ArS)_3CCH_3$ AND RELATED COMPOUNDS IN CF_3CO_2D

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In the course of our investigation on the chemistry of aryl trithioorthoacetates $(ArS)_3CCH_3$[1], we have found that the methyl group can undergo H-D exchange quite easily in trifluoroacetic acid-d at room temperature, affording almost quantitative yields of $(ArS)_3CCD_3$. We now wish to communicate this and related results.

$$(ArS)_3CCH_3 \xrightarrow[\text{2. evapn.}]{\text{1. } CF_3CO_2D \text{ (rT)}} (ArS)_3CCD_3 \qquad (1)$$

The proton nmr spectrum[2] of phenyl trithioorthoacetate $(PhS)_3CCH_3$[3] in $CDCl_3$ shows a singlet (3 H) at δ 1.38 for the methyl group. This peak appears in trifluoroacetic acid at δ 2.90 and disappears almost completely and instantaneously on dissolution into trifluoroacetic acid-d. By evaporation of a solution of $(PhS)_3CCH_3$ in CF_3CO_2H at room temperature or by pouring it onto crashed ice, the material was recovered quantitatively. Dissolution of this compound (1 g) into CF_3CO_2D (5 ml) and subsequent evaporation gave quantitative yield of $(PhS)_3CCD_3$. This material, the deuterium content of which was estimated to be more than 90 % by nmr integration in $CDCl_3$ and also from mass spectrum, was converted back to $(PhS)_3CCH_3$ by dissolving it into CF_3CO_2H and confirmed by mixture melting point. Starting with p-tolyl[1] and p-anisyl[1] derivatives the same procedure afforded corresponding deuterated compounds, $(p\text{-}CH_3C_6H_4S)_3CCD_3$ and $(p\text{-}CH_3OC_6H_4S)_3CCD_3$, in quantitative yields, the deuterium content being more than 90 %.

This H-D exchange reaction can also be applicable to dithioacetals of various dialkyl and alkyl aryl ketones, although the exchange becomes somewhat slower than the case of trithioorthoacetates and it takes several minutes for the exchange to exceed over 90 %. For example, di-p-tolyl dithioacetal of acetone, diphenyl dithioacetal of diethyl ketone and di-p-tolyldithioacetal of acetophenone were converted, according to this method, to $(p\text{-}CH_3C_6H_4S)_2C(CD_3)_2$ (yield 87 %, D-content 83 %), $(PhS)_2C(CD_2CH_3)_2$ (74 %, 92 %) and $(p\text{-}CH_3C_6H_4\text{-}S)_2CPhCD_3$ (72 %, 90 %), respectively.

Mechanistically, the present H-D exchange reaction seems very interesting. A large downfield shift observed for methyl protons of $(PhS)_3CCH_3$ on changing solvents from $CDCl_3$ (δ 1.38) to CF_3CO_2H (δ 2.90) suggests that this compound is ionized completely in trifluoroacetic acid[4] according to equation 2.

$$(ArS)_3CCH_3 \underset{rT}{\overset{TFA}{\rightleftharpoons}} (ArS)_2C^+CH_3 \quad + \quad ArS^- \qquad (2)$$

$$(ArS)_2C^+CH_3 \rightleftharpoons (ArS)_2C{=}CH_2 \quad + \quad H^+ \qquad (3)$$

Similar phenomena can be seen for all the other trithioorthoacetates and dithioacetals[5]. It seems very likely that these compounds are existing wholly as ionic species (probably as ion pairs) in trifluoroacetic acid and go back to the covalent species on evaporation of the solvent. The H-D exchange probably occurs via olefins (equation 3).

This reaction may be conveniently used for preparation of deuterated compounds. For instance, $ArCH_2CD_3$ may be obtained by desulfurization (Raney-Ni) of $(ArS)_2CArCD_3$. Synthesis of $ArCOCD_3$ and derivatives therefrom seems particularly interesting.

REFERENCES AND NOTES

1. M. Hojo and R. Masuda, J. Org. Chem., 40, No. 7 (1975).
2. Recorded on a 60 MHz Hitachi R-24 spectrometer.
3. G. A. Wildschut, H. J. T. Bos, L. Brandsma and J. F. Arens, Monatsh. Chem., 98, 1043 (1967).
4. Equimolar mixtures of ketene dithioacetals $(ArS)_2C{=}CH_2$ and thiophenols ArSH give essentially the same nmr spectra in trifluoroacetic acid as those of the corresponding $(ArS)_3CCH_3$.
5. Dithioacetal of acetaldehyde $(PhS)_2CHCH_3$ gives almost the same nmr spectrum in CF_3CO_2H as that in $CDCl_3$. No ionization occurs.