

FACILE H-D EXCHANGE OF METHYL HYDROGENS OF (ArS)₃CCH₃ AND RELATED
COMPOUNDS IN CF₃CO₂D

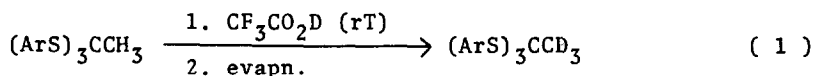
Masaru Hojo, Ryōichi Masuda, Kōichi Yamane and Harumi Takahashi

Department of Industrial Chemistry, Faculty of Engineering,

Kobe University, Rokkodai, Kobe, 657, Japan

(Received in Japan 15 April 1975; received in UK for publication 25 April 1975)

In the course of our investigation on the chemistry of aryl trithioorthoacetates (ArS)₃CCH₃¹, 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)₃CCD₃. We now wish to communicate this and related results.

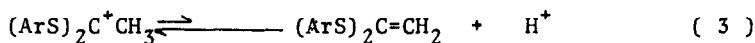
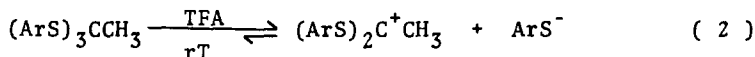


The proton nmr spectrum² of phenyl trithioorthoacetate (PhS)₃CCH₃³ in CDCl₃ shows a singlet (3 H) at δ 1.38 for the methyl group. This peak appears in trifluoroacetic acid at δ 2.90 and disappears almost completely and instantaneously on dissolution into trifluoroacetic acid-d. By evaporation of a solution of (PhS)₃CCH₃ in CF₃CO₂H at room temperature or by pouring it onto crashed ice, the material was recovered quantitatively. Dissolution of this compound (1 g) into CF₃CO₂D (5 ml) and subsequent evaporation gave quantitative yield of (PhS)₃CCD₃. This material, the deuterium content of which was estimated to be more than 90 % by nmr integration in CDCl₃ and also from mass spectrum, was converted back to (PhS)₃CCH₃ by dissolving it into CF₃CO₂H and confirmed by mixture melting point. Starting with *p*-tolyl¹ and *p*-anisyl¹ derivatives the same procedure afforded corresponding deuterated compounds, (*p*-CH₃C₆H₄S)₃CCD₃ and (*p*-CH₃OC₆H₄S)₃CCD₃, 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*-tolyl dithioacetal of acetophenone were converted, according to this method, to $(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{C}(\text{CD}_3)_2$ (yield 87 %, D-content 83 %), $(\text{PhS})_2\text{C}(\text{CD}_2\text{CH}_3)_2$ (74 %, 92 %) and $(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{CPhCD}_3$ (72 %, 90 %), respectively.

Mechanistically, the present H-D exchange reaction seems very interesting. A large downfield shift observed for methyl protons of $(\text{PhS})_3\text{CCH}_3$ on changing solvents from CDCl_3 (δ 1.38) to $\text{CF}_3\text{CO}_2\text{H}$ (δ 2.90) suggests that this compound is ionized completely in trifluoroacetic acid⁴ according to equation 2.



Similar phenomena can be seen for all the other trithioorthoacetates and dithioacetals⁵. 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 $(\text{ArS})_2\text{CArCD}_3$. 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 $(\text{ArS})_2\text{C}=\text{CH}_2$ and thiophenols ArSH give essentially the same nmr spectra in trifluoroacetic acid as those of the corresponding $(\text{ArS})_3\text{CCH}_3$.
5. Dithioacetal of acetaldehyde $(\text{PhS})_2\text{CHCH}_3$ gives almost the same nmr spectrum in $\text{CF}_3\text{CO}_2\text{H}$ as that in CDCl_3 . No ionization occurs.