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DITHIOACETIC ACID TRIMERS.

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In a recent book, S. Oae reports unpublished results according to which dithioacetic acid (I) on standing for a prolonged period of time affords tetramethylhexathiaadamantane (II) [1]. Working on dithio-acids and -esters for several years, we have observed that well-purified dithioacetic acid forms spontaneously colourless crystals when standing for weeks in a refrigerator ; the remaining solution affords, on vacuum evaporation, further crystalline material ; total yields as high as 60 % were noted. ^1H N.M.R. and mass spectra show the presence in the first crop of tetramethylhexathiaadamantane (II) as a minor product (ca. 5 %).

II N.M.R. ($CDCl_3$) : δ_{CH_3} = 2.08 ppm (lit. 2.1) [2]

Mass spectrum m/e = 300 ($C_8H_{12}S_6$)

The second fraction of crystalline material and the main part of the first one are found to be (elemental analysis, N.M.R. and mass data) mixtures of the two isomers (III) and (IV) of trimeric dithioacetic acid [3] ; the symmetrical trithiane (III) was the major component of the less soluble fraction while the unsymmetrical trithiane (IV) was the major product of the more soluble fraction ; on slow crystallisation in carbon tetrachloride, monocrystals (M.p 88-90° with decomposition) containing both isomers in the same proportions were obtained. The two isomers were not separated and on chromatography or distillation they give back the monomeric dithioacid.

Mass spectrum : m/e : 276 (M = $C_6H_{12}S_6$), 243 (M-SH), 184 (2 M/3), 151 (2 M/3 - SH), 92 (M/3), 59 (CH_3CS).

Analysis. $C_6H_{12}S_6$: Calc.% : C 26,06 H 4,37 S 69,57
Found. : 26,12 4,41 69,48

Proton N.M.R. spectrum ($CDCl_3$, δ_{TMS} = 0)

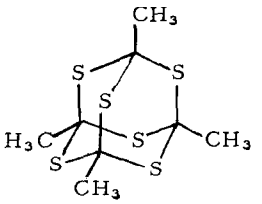
III $\delta(CH_3)_{eq}$ = 2,03 (d) $\delta(SH)_{ax}$ = 3,70 (q) ^4J = 1,35 Hz

IV $\delta(CH_3)_{eq}$ = 2,19 (d) $\delta(SH)_{ax}$ = 3,20 (q) ^4J = 1,35 Hz

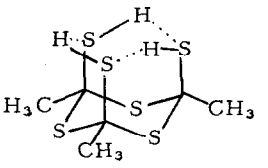
$\delta(CH_3)_{ax}$ = 2,22 (d) $\delta(SH)_{eq}$ = 3,13 (q) ^4J = 0,55 Hz

I.R. Intense doublet at 2550-2530 cm^{-1} (HS).

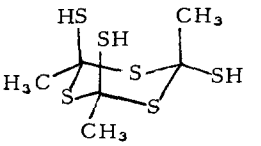
I CH_3CS_2H



II



III



IV

The assignment of the conformations shown here for the individual isomers (III) and (IV) is based on the low field resonance observed for the HS protons in the symmetrical compound compared to those of the unsymmetrical one ; the axial and equatorial thiol groups in this unsymmetrical trithiane (IV) give signals nearly at the same shift and similar to that reported for the dithioformic acid trimer (3.25 ppm)[4]. Hence there appears to be no configurational reason which can account for the low field δ_{SH} value in (III) ; however in the case of three axial thiol groups it is possible to postulate three intramolecular hydrogen bonds with formation of a six membered ring (and this is fully consistent with the known influence of hydrogen-bonding on chemical shift) ; this possibility disappears as soon as one SH group becomes equatorial as in (IV) and only much weaker hydrogen-bonding then occurs : the conformation of (IV) follows from the comparison of the long range couplings between the methyl and the thiol groups (two methyls equatorial with ^4J = 1.35 Hz as in (III) and one axial with ^4J = 0.55 Hz).

The dithioacetic acid (I) was prepared in 55 % yield according to the previously described method[5].

REFERENCES

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