

SILICON DERIVATIVE OF DEHYDRACETIC ACID

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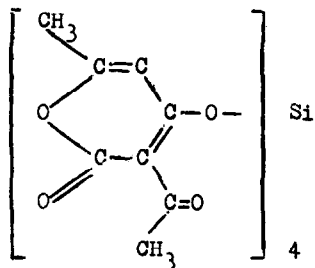
Hexacoordinate silicon chelates result from the interaction of SiCl_4 with acetylacetone and ethyl acetoacetate⁽¹⁾. The aim of the present investigation is to find out whether dehydracetic acid, a β -diketone closely related to these two compounds, interacts similarly with SiCl_4 .

When 0.3 mole dehydracetic acid and 0.1 mole SiCl_4 were mixed at room temperature in 100 cc dry CHCl_3 in a moisture-free atmosphere, no immediate reaction was noticed. The mixture turned yellow within an hour and dark red overnight; the colour formation was accompanied by development of gaseous HCl. Dark red crystals were precipitated by addition of 400 cc ether. (When the interaction of dehydracetic acid and SiCl_4 was carried out in ether, red crystals formed overnight under a yellow supernatant.) The crystals were filtered off, redissolved in CHCl_3 and reprecipitated by ether. m.p. 116-117. The material contains no chlorine; the composition and molecular weight (determined by cryoscopy with CHBr_3 as solvent) are in agreement with the formula $\text{C}_{32}\text{H}_{28}\text{O}_{16}\text{Si}$ (Calc. C, 55.14, H, 4.03, Si, 4.03, mol. wt. 696; found; C, 54.82, H, 4.06, Si, 4.08, mol. wt. 650). The crystals remain red when kept in a desiccator, but turn yellow soon after exposure to moisture. Their solution in CHCl_3 , CHBr_3 , ethanol and dimethylformamide is red, while that in aqueous KOH is bright yellow like the solution of tris(2,4-pentanedione)siliconium chloride⁽¹⁾.

The IR-spectrum (in KBr) of the substance is identical with that of dehydracetic acid except for a broad band at 1080 cm^{-1} , which corresponds to the Si-O-C bond. Its UV-spectrum (in CHCl_3) displays the peak at $310\text{ m}\mu$ of the parent compound and in addition a peak at $440\text{ m}\mu$ ($\log = 3.15$). The NMR-spectrum of both dehydracetic acid and its interaction product with SiCl_4 show resonances with chemical shifts at 2.25, 2.60 and 6.00 ppm (in CDCl_3).

The introduction of an ethyl group at the C4 position of dehydracetic acid was found to cause little change in either the IR, UV or NMR spectrum^(2,3,4). It may thus be inferred from the present findings that the dehydracetic acid binds to silicon without undergoing ring opening and that silicon, like the ethyl group, is bound at the C4 position. According to Pike and Luongo, the neutral unchelated acetoxy-silyl ester of the normal enolate of

acetylacetone shows no absorption in the 1500-1600 and 650-700 cm^{-1} regions. The fact that no new bands are formed in the spectrum of dehydracetic acid in these regions upon binding to silicon indicates that the compound formed contains no chelates. Thus its probable structure is



References:

1. W. Dilthey, Ber. 36, 926 (1903).
2. S. Forsen and M. Nilsen, Arkiv Kemi 17, 523 (1961).
3. E. E. Royals and C. Leffingwell, J. Org. Chem. 30, 1255 (1965).
4. J. A. Berson, J. Amer. Chem. Soc. 74, 5172 (1952).
5. R. M. Pike and R. L. Luongo, J. Amer. Chem. Soc. 87, 1403 (1965).