A Nitrogen Analogue of Deltic Acid

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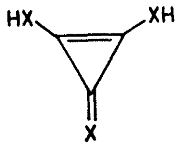
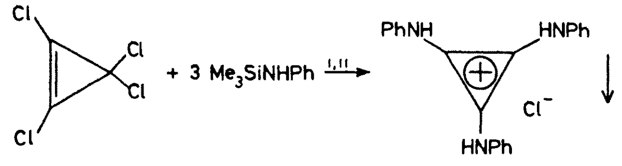
Summary The synthesis of dianilinophenyliminocyclopropene (**1b**), the first nitrogen analogue of deltic acid, has been achieved by a transamination reaction between tetrachlorocyclopropene (**2**) and trimethylsilylaniline (**3**), followed by deprotonation of the primary product, the trisanilinocyclopropenium salt (**4**)

The elegant synthesis of deltic acid, (**1a**) by Eggerding and West[1] is a major achievement of recent three-membered ring chemistry While further exploration of the chemistry of (**1a**) has been limited by its lack of accessibility, systems analogous to (**1**) with donor functions X other than oxygen have remained totally inaccessible We now report a simple, high-yield synthesis of (**1b**), the first aza-analogue of deltic acid



(**1**) a, X = O
b, X = NPh

A suitable precursor for (**1b**) was obtained by applying a transamination technique which we had previously[2] devised for the synthesis of mono-, bis-, and tris-dialkylaminocyclopropenium salts (Scheme) The transamination product (**4**) represents the first tris(mono-organylamino)cyclopropenium salt It was obtained in near-quantitative yield



(2) (3) (4)

SCHEME i, CH_2Cl_2, room temperature, 6 h; ii, $-3\ Me_3SiCl$.

under these conditions as a stable, CH_2Cl_2-insoluble salt of m.p. 207 °C (decomp.); i.r. (KBr) 1540 br vs cm^{-1} [characteristic ring vibration $(E')^3$]; u.v. (MeCN) λ_{max} 270 nm (log ϵ 4·41); ^1H-n.m.r. δ (CD_3CN/Me_4Si standard) 10·1 (brs, 3H, N–H) and 7·3 (s, 15H).

Mass spectroscopic studies on (**4**) indicate ready loss of HCl with formation of the cation radical of (**1b**) as the parent peak. Dehydrohalogenation of (**4**) can also be effected in solution according to equation (1). Owing to the thermal instability of (**1b**) and the heterogeneous reaction medium a prolonged reaction time at low temperature must be allowed.

$$(\mathbf{4}) + NaN(SiMe_3)_2 \xrightarrow[-78\ ^\circ C,\ 12\ h]{\text{tetrahydrofuran}} (\mathbf{1b}) + NaCl + HN(SiMe_3)_2 \quad (1)$$

Low-temperature work-up yields the colourless imine (**1b**) in 72% yield, with m.p. 130 °C (decomp.); i.r. (KBr) 1910 and 1510 br vs cm^{-1}; u.v. ($CHCl_3$) λ_{max} 271 nm (log ϵ 4·39); m.s. (70 eV) *m/e* (rel. intensity) 622 (M_2^+, 87%), 529 ($M_2^+ - Ph - NH_2$, 100), 311 (M^+, 4), and 208 ($M^+ - PhNC$, 10). The ^{13}C-n.m.r. spectrum of (**1b**) indicates rapid intra- or inter-molecular proton exchange: apart from the sub-spectrum of the equivalent anilino groups it shows only one singlet for the cyclopropenium C-atoms at δ 115·0 p.p.m. (CD_3CN/Me_4Si standard).

The imine (**1b**) can be stored at −30 °C for weeks without decomposition. At ambient temperatures it decomposes within several days into phenylisonitrile and an orange-yellow substance of as yet unknown structure. Compound (**1b**) is quantitatively reconverted into (**4**) by HCl gas and methylating agents give mixtures of the mono-, di-, and tri-methylated salt of (**4**). As an aza-analogue of deltic acid (**1b**) should be capable of further deprotonation by strong base.

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