

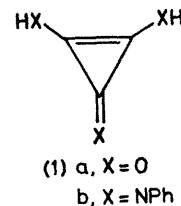
A Nitrogen Analogue of Deltic Acid

By ROBERT WEISS* and MARION HERTEL

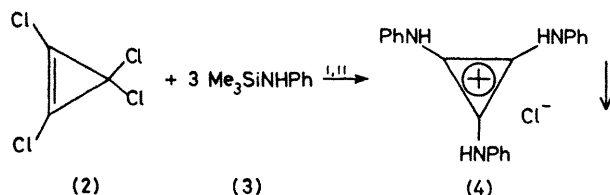
(*Institut für Organische Chemie der Universität Erlangen-Nürnberg, D-8520 Erlangen, W. Germany*)

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 West¹ 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.

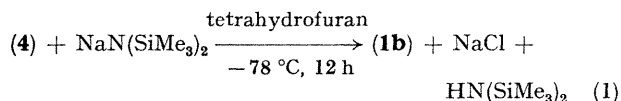


A suitable precursor for (**1b**) was obtained by applying a transamination technique which we had previously² devised for the synthesis of mono-, bis-, and tris-dialkylaminocyclopropenium salts (Scheme). The transamination product (**4**) represents the first tris(mono-organylamino)cyclopropenium salt. It was obtained in near-quantitative yield.

SCHEME i, CH_2Cl_2 , room temperature, 6 h; ii, $-3 \text{ Me}_3\text{SiCl}$.

under these conditions as a stable, CH_2Cl_2 -insoluble salt of m.p. 207°C (decomp.); i.r. (KBr) $1540 \text{ br vs cm}^{-1}$ [characteristic ring vibration (E')³]; u.v. (MeCN) $\lambda_{\text{max}} 270 \text{ nm}$ ($\log \epsilon 4.41$); $^1\text{H-n.m.r.}$ δ ($\text{CD}_3\text{CN}/\text{Me}_4\text{Si}$ 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.



Low-temperature work-up yields the colourless imine (1b) in 72% yield, with m.p. 130°C (decomp.); i.r. (KBr) 1910 and $1510 \text{ br vs cm}^{-1}$; u.v. (CHCl_3) $\lambda_{\text{max}} 271 \text{ nm}$ ($\log \epsilon 4.39$); m.s. (70 eV) m/e (rel. intensity) 622 (M_2^+ , 87%), 529 ($M_2^+ - \text{Ph-NH}_2$, 100), 311 (M^+ , 4), and 208 ($M^+ - \text{PhNC}$, 10). The $^{13}\text{C-n.m.r.}$ spectrum of (1b) indicates rapid intra- or inter-molecular proton exchange: apart from the subspectrum of the equivalent anilino groups it shows only one singlet for the cyclopropenium C-atoms at $\delta 115.0 \text{ p.p.m.}$ ($\text{CD}_3\text{CN}/\text{Me}_4\text{Si}$ standard).

The imine (1b) can be stored at -30°C for weeks without decomposition. At ambient temperatures it decomposes within several days into phenylisocyanide 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 trimethylated salt of (4). As an aza-analogue of deltic acid (1b) should be capable of further deprotonation by strong base.

We are indebted to the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for generous support of this work.

(Received, 3rd December 1979; Com. 1258.)

¹ D. Eggerding and R. West, *J. Amer. Chem. Soc.*, 1976, **98**, 3641.

² R. Weiss and K. Schlöter, *Tetrahedron Letters*, 1975, 3491; R. Weiss, *ibid.*, 1979, 3295.

³ Z. Yoshida, *Topics in Current Chem.*, 1973, **40**, 47.