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(7) Dysidin was isolated from the sponge *Dysidea herbacea*. Interestingly blue-green algae are associated with this sponge.
(8) Using the program CONGEN 24 gross structures were assembled from the following fragments: R_1 = **2b**, R_2 = **2a** with one Me group on the nitrogen, two XCH_2X groups with no protons on the X atoms, one >C=CH– group, one MeO—C=CH– group, and a chlorine atom. Only one of these 24 structures satisfactorily explains the degradation of malyngamide A to **8**, **9**, and **10**. We thank T. Varkony and C. Djerassi for this determination.
(9) Oil; mass spectrum *m/e* (rel intensity) 401 (1), 399 (4, M$^+$), 384 (3), 364 (11), 332 (8), 315 (7), 259 (26), 257 (75), 222 (22), 205 (20), 203 (57), 158 (35), 146 (53), 143 (100), 111 (41); high resolution mass spectrum *m/e* 399.2503 (calcd for $C_{22}H_{38}{}^{35}ClNO_3$, 399.2540); UV (MeOH) λ_{max} 212 nm (ϵ 3900) assigned to the $\pi \rightarrow \pi^*$ transition for the β,γ-unsaturated ketone carbonyl; IR (neat) 1718, 1655, 980 cm^{-1}; ^{1}H NMR δ 6.07 (1 H, br s), 5.50 (2 H, br t), 4.24 (2 H, br s), 3.33 (3 H, s), 3.16 (2 H, s, on 1 H, br quintet), 2.92 (3 H, s), 2.34 (4 H, br m), 2.15 (3 H, s, on 2 H, br m), 1.26 (12 H, br s with low-field sh), 0.88 (3 H, br t, J = 7 Hz). Two signals in the ^{1}H NMR spectrum are doubled in a 6:1 ratio (δ 6.07/6.11, assigned to =CHCl, and 2.92/2.83, assigned to the NCH_3 for the two conformers); irradiation at δ 2.92 produces a 19% positive NOE in the signal at δ 6.07 and a 5% negative NOE in the methylene signal at δ 4.24.
(10) Oil; mass spectrum *m/e* (rel intensity) 385 (>1), 312 (2), 241 (12), 200 (23), 187 (19), 143 (25); high resolution mass spectrum *m/e* 385.2838 (M$^+$; calcd for $C_{21}H_{39}NO_5$, 385.2828), 312.2511 (calcd for $C_{18}H_{34}NO_3$, 312.2539), 241.2173 (calcd for $C_{15}H_{29}O_2$, 241.2168), 200.0931 (calcd for $C_9H_{14}NO_4$, 200.0923), 187.0847 (calcd for $C_8H_{13}NO_4$, 187.0845); UV (MeOH) λ_{max} 213 nm (ϵ 5400) → 271 (11 000), 214 (7900) in methanolic NaOH; IR 1735, 1720 (sh), 1650 cm^{-1}; ^{1}H NMR δ 4.24 (2 H on C-4, s), 3.71 (3 H, s, ester OMe), 3.46 (2 H on C-2, s), 3.28 (3 H, s), 3.05 (1 H, br quintet), 3.02 (3 H, s, *N*-Me), 2.30 (2 H, br t, J = 7 Hz), 1.65–1.20 (20 H, br m), 0.83 (3 H, br t, J = 7 Hz).
(11) Identified by high resolution mass spectrum: *m/e* 385.3169 (M$^+$, calcd for $C_{22}H_{43}NO_4$, 385.3192), 312.2874 (calcd for $C_{19}H_{38}NO_2$, 312.2903), 241.2173 (calcd for $C_{15}H_{29}O_2$, 241.2168), 200.1296 (calcd for $C_{10}H_{18}NO_3$, 200.1287), 187.1198 (calcd for $C_9H_{17}NO_3$, 187.1208).

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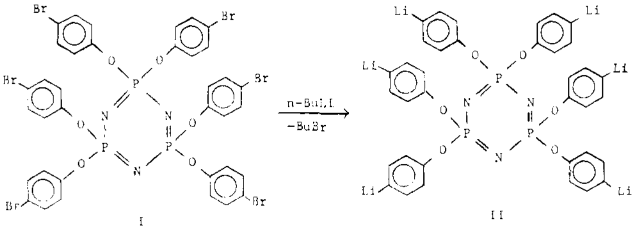
Preparation of $[NP(p\text{-}OC_6H_4Li)_2]_3$ by Metal-Halogen Exchange, and Its Reactions with Electrophiles

Sir:

The reactions of cyclic and polymeric *halo*phosphazenes with organolithium reagents have been studied extensively,[1-3] but the reactions of organometallic reagents with cyclic and polymeric *organo*-functional phosphazenes have not been explored in detail. Of particular interest to us were reactions that could yield carbanionic species bound directly to phosphazene cyclic and polymeric compounds. Such reactive intermediates could be used to synthesize a wide range of new cyclic and high polymeric phosphazenes not accessible by other synthetic routes, including those that might form unusual ligands for transiton metals.

We have found that hexa(p-bromophenoxy)cyclotriphosphazene (I) undergoes a high yield metal-halogen exchange reaction with n-butyllithium to yield the hexalithio derivative (II). The reaction conditions employed involved a rapid addition of n-butyllithium (1.6 M in hexane) in a 15% excess to a tetrahydrofuran solution of I at −40 °C.



I

II

The presence of II was confirmed by its reactions at −40 °C with electrophiles, such as deuterium oxide, carbon dioxide, chlorodiphenylphosphine, and triphenyltin chloride to yield the following derivatives: $[NP(p\text{-}OC_6H_4D)_2]_3$ (III), $[NP(p\text{-}OC_6H_4COOH)_2]_3$ (IV), $\{NP[p\text{-}OC_6H_4P(C_6H_5)_2]_2\}_3$ (V), and $\{NP[p\text{-}OC_6H_4Sn(C_6H_5)_3]_2\}_3$ (VI). All of these compounds were identified by ^{31}P NMR spectra, infrared spectra, and chemical analysis. The position of lithium incorporation on the aromatic ring was confirmed by the ^{13}C NMR spectrum of compound III which revealed both the presence of a triplet structure and a decrease in the resonance signal for the carbon at the para position of the aromatic unit when compared with the ^{13}C NMR spectrum of $[NP(OC_6H_5)_2]_3$.[4] The absence of significant skeletal cleavage during metalation is a considerable advantage for the use of such processes in phosphazene high polymer syntheses.

The binding of metal complexes to phosphazene compounds is of structural, catalytic, and potential biomedical importance.[5,6] This reaction system possesses a capacity for the binding of metals both through reactions of II with metal halides, as demonstrated by the synthesis of compound VI, and through the reactions of compound V with metal complexes. To illustrate this second reaction pathway, V was allowed to react with $H_2Os_3(CO)_{10}$ (VII), a compound which has been demonstrated previously to react with tertiary phosphines to yield monosubstituted phosphine osmium cluster compounds, $H_2Os_3(CO)_{10}(PR_3)$.[7] The high reactivity of this osmium cluster (VII) was ascribed to a metal-metal double bond.[8] When compound V was allowed to react with a deficiency of VII at 25 °C in methylene chloride solvent, the expected color change from violet to yellow was observed. Furthermore infrared spectral comparisons of the carbonyl stretching regions for the osmium complex derived from triphenylphosphine and that derived from V confirmed the existence of metal binding through the phosphine residues of V rather than through the skeletal nitrogen atoms.

Experiments are now underway in our laboratory to extend these small molecule cyclic model reactions to high polymeric phosphazenes.

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