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ON THE REACTION OF (VINYLIMINO)PHOSPHORANES AND RELATED COMPOUNDS[1] SYNTHESIS AND PROPERTIES OF NOVEL 1,6-METHANOCYCLODECA[b]CYCLOHEPTA[d]PYRROLE

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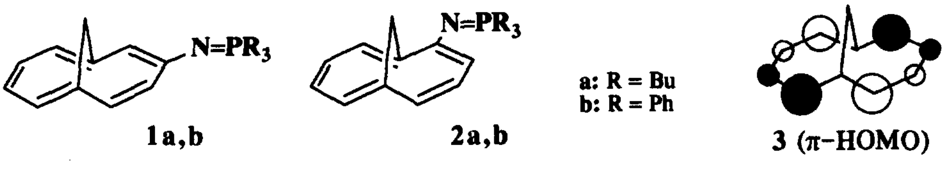
Summary: The title compound was synthesized by thermal reaction of 3-phosphoranylideneamino-1,6-methano[10]annulene with 2-chlorotropone in a single step. The examination of ^{1}H NMR spectrum revealed that there is little contribution of peripheral 18-π electron conjugation, but it is rather composed of 1-azaazulene and methano[10]annulene moieties.

During the course of our investigation in the field of (vinylimino)phosphorane, we were confronted with the preparation of 1-azaazulene[2] and their vinylogues, methanocycloundeca[b]pyrroles.[3] Previously, we have reported the preparation of novel 3-phosphoranylideneamino- and 2-phosphoranylideneamino-1,6-methano[10]annulene (1a,b) and (2a,b), and their reaction with α,β-unsaturated ketones.[4] The compounds 1a and 2a, prepared in situ, are the first examples of (vinylimino)phosphoranes, the vinyl group of which is a part of aromatic perimeter, to undergo an enamine-type alkylation and following aza-Wittig reaction giving pyridine ring system.[4] Although the syntheses and aromatic characters of 1,6-methano[10]annulenes condensed with benzene(s)[5,6] and heterocycles[7] have been studied, azulene-annelated compound thus far obtained is, to our best knowledge, a peripheral 18-π electronic diatropic compound, azuleno[2,1-b]-4,9-methano[11]annulenium ion.[8] In search for precise reactivities of 1,6-methano[10]annulene nucleus (3) of 1a and 2a as well as interests in the 1,6-methano[10]annulene condensed with nonbenzenoid aromatic π-system,[9] we investigated the reaction of 1a and 2a with 2-chlorotropone (4) and spectroscopic properties of the resulting 1,6-methanocyclodeca[b]cyclohepta[d]pyrrole (8).

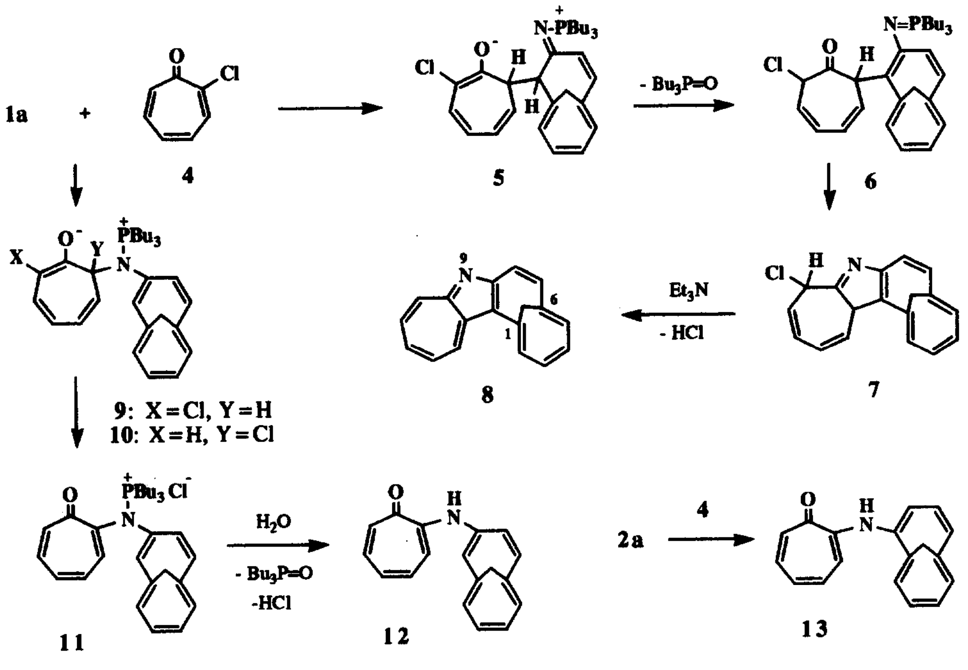


Scheme 1.

The compound 1a[4] was prepared in situ by the Staudinger reaction[10] of 3-azido-1,6-methano[10]annulene (106 mg, 0.58 mmol) with tributylphosphine (138 mg, 0.64 mmol) in dry toluene (4 ml) at room temperature for 1 h.[4] To this solution was added 4 (122 mg, 0.47 mmol) and triethylamine (292 mg, 2.9 mmol), and the mixture was heated under reflux for 5h to give 8 and 3-(2-troponyl)amino-1,6-methano[10]annulene (12) in 5% and 23% yields (based on 4 used), respectively, after separation by TLC on silica gel (hexane/AcOEt: 1/1). On the contrary, the reaction of 4 with 2a, which was prepared in situ from 2-azido-1,6-methano[10]annulene and tributylphosphine under the conditions similar to the case of 1a, gave only 2-(2-troponyl)amino-1,6-methano[10]annulene (13) in 8% yield (Scheme 2). The evidence for the structures of new compounds, 8, 12, and 13 was provided by spectral data.[11,12]

The postulated pathways for the formation of 8 and 12 (or 13) are also shown in Scheme 2.[8] The enamine-type alkylation of the iminophosphorane 1a on C-7 of 4 gives the intermediate 5. The hydrogen migration in 5 regenerates iminophosphorane 6, which undergoes intramolecular aza-Wittig reaction and following dehydrochlorination to give 8. On the other hand, nucleophilic attack of the imino-nitrogen also occurs on C-2 or C-7 of 4 to give 9 or 10. The nucleophilic substitution onto tropone carrying mobile substituent at C-2 have been known to take place either on C-2 (normal substitution) or C-7 (abnormal substitution) to give 2-substituted tropone.[13] Thus, it is not concluded a priori whether 9 or 10 is prefered. The hydrogen transfer in 9 and following dechlorination or direct dechlorinataion of 10 gives 11, the hydrolysis of which results in the formation of 12 under workup conditions. The compound 13 is also produced in a sumilar pathway.

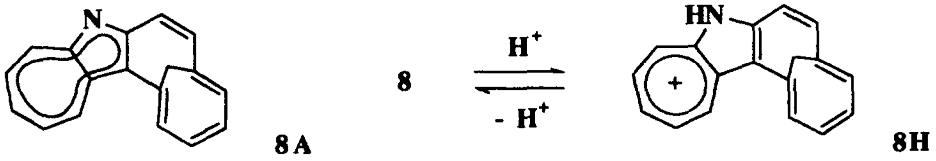
One may consider that the enamine alkylation leading to 5 is frontier orbital controlled and substitution reaction giving 9 (or 10) is charge controlled reaction.[14] Regarding 1,6-methano[10]annulene, the substantial transannular interaction between the



Scheme2.

bridgehead C-1 and C-6 positions permits description of it as homonaphthalene, and leads to a large π-HOMO coefficient at C-2 than at C-3 as depicted in 3 (Scheme 1),[15,16] thereby facilitating nucleophilic attack at the former. As previously reported, the ^{13}C NMR spectra revealed that the signals of C-2 in 1b (δ 118.3) and C-3 in 2b (δ 116.6) are shifted toward upfield by 10.9 ppm and 10.0 ppm, respectively,[4] as compared to the corresponding carbon atoms of 1,6-methano[10]annulene (C-2: δ 129.2; C-3: δ 126.6).[17] Thus, it is suggested that the intrinsic large π-HOMO coefficient of C-2 is much enhanced by introduction of iminophosphorane moiety in 1a, as compared to the intrinsic small one of C-3 in 2a. Consequently, the enamine alkylation process leading to 8 could compete with substitution reaction giving 12 for 1a. In the case of 2a, only substitution reaction giving 13 occurred.

Unambiguous proton assignment for 8 provides no indication of an equilibrium between 8 and its norcaradiene tautomer.[12] The average chemical shift (δ_{av}=7.45) of methano-[10]annulene moiety of 8 is slightly shifted to the lower field (0.25 ppm) than that of 2,3-benzo-1,6-methano[10]annulene (δ_{av}=7.20).[5] The average chemical shift (δ_{av}=8.55) of azaazulene moiety also shifted to the lower field (0.43 ppm) than that of 1-azaazulene δ_{av}=8.13).[18] These are partially due to the magnetic anisotropy from the adjacent ring system to each other. The weakening of the diamagnetic ring current in the methano-[10]annulene ring of 8 expected as a result of 1-azaazulene-annelation is most clearly manifested in the signals of the bridge protons (δ_{av}=0.75) for they are shielded similarly to that in 2,3-benzo-1,6-methano[10]annulene (δ_{av}=0.66)[5], but less shielded than that of 1,6-methano[10]annulene.[19] More finding such as the relative large vicinal coupling constants, J_{3-4} (10.25 Hz) and J_{7-8} (10.26 Hz), as compared to J_{2-3} (6.34 Hz) and J_{4-5} (6.84 Hz) indicates a double-bond fixation in methano[10]annulene moiety. On the contrary, the same vicinal coupling constant (J=9.7 Hz) for J_{10-11}, J_{11-12}, J_{12-13}, and J_{13-14} in azaazulene moiety suggests that the π bonds in azaazulene moiety are delocalized as depicted in 8A. The UV spectrum is consistent with prolonged conjugation as in the case of benzo[e]cyclohept[b]indole [λ_{max} (log ε) 258 (4.26), 315 (4.67), 328 (4.68), 342 (4.55), 358 (3.99), 377 (3.96), 388 (3.99), 404 (3.28), 560 (2.87), 610 (2.80)].[20] The hypsochromic shift is observed in acidic media,[12] being in good accordance with the behavior of 1-azaazulene. The chemical shifts of ^{1}H NMR spectrum in $CDCl_3$-CF_3CO_2H exhibited slight down field shift (δ_{av}=0.13) of peripheral protons of methano[10]annulene moiety and remarkable down field shift (δ_{av}=0.3-0.4) of azaazulene moiety. Accordingly, the protonation onto 8 occurred at the nitrogen atom in acidic solution, and the contribution of the canonical structure



Scheme 3.

8H to the resonance hybrid becomes important.

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12. Spectral data of new compounds: 8: dark green solid; mp 135-138 °C (decomp); ^{1}H NMR (CDCl$_3$, 400 MHz), δ=0.14 and 1.35 (1H each, J=9.77 Hz, methano bridge), 7.54 (1H, d, J=6.34 Hz, H-2), 7.41 (1H, dd, J=10.25, 6.34 Hz, H-3), 7.29 (1H, dd, J=10.25, 6.84 Hz, H-4), 7.09 (1H, d, J=6.84 Hz, H-5), 7.76 (1H, d, J=10.26 Hz, H-7), 7.61 (1H, d, J=10.26 Hz, H-8), 9.51 (1H, d, J=9.77 Hz, H-10), 8.03 (1H, td, J=9.7, 3.42 Hz, H-11), 8.11 (1H, t, J=7.77 Hz, H-12), 8.03 (1H, td, J=9.77, 3.42 Hz, H-13), 9.10 (d, J=9.77 Hz, H-14); ^{1}H NMR (CDCl$_3$-CF$_3$CO$_2$H, 400 MHz) δ=0.14 and 1.35 (1H each, d, J=9.77 Hz, methano bridge), 7.64 (1H, d, J=6.69 Hz, H-2), 7.53 (1H, d, J=10.26, 6.69 Hz, H-3), 7.44 (1H, d, J=10.26, 6.96 Hz, H-4), 7.26 (1H, d, J=6.96 Hz, H-5), 7.36 (1H, d, J=10.62 Hz, H-7), 8.01 (1H, d, J=10.62 Hz, H-8), 9.81 (1H, dd, J=9.81, 1.11 Hz, H-10), 8.44-8.55 (3H, m, H-11, 12, and 13), 9.16 (1H, d, J=9.16 Hz, H-14); λ_{max} (log ε) in EtOH, 234 (4.34), 272 (4.15, sh), 304 (4.31), 322 (4.35), 355 (4.15, sh), 430 (3.79), 556 (2.85); λ_{max} (log ε) in EtOH-CF$_3$CO$_2$H, 224 (4.31), 256 (4.34), 279 (4.24, sH), 295 (4.21, sh), 327 (4.07), 368 (4.03), 454 (3.85). 12: oil; ^{1}H NMR (CDCl$_3$, 90 MHz) δ=-0.11 (2H, s, methano bridge), 6.78-7.50 (11H, m), 7.70 (1H, d, J=10.2 Hz), 9.12 (1H, broad s, NH); IR (CHCl$_3$) 1630, 1590 cm^{-1}. 13: oil; ^{1}H NMR (CDCl$_3$, 90 MHz) δ=-0.38 (1H, d, J=9.5 Hz, methano bridge), -0.02 (1H, d, J=9.5 Hz, methano bridge), 6.80-7.70 (12H, m), 9.16 (1H, broad s, NH); IR (CHCl$_3$) 1610, 1550 cm^{-1}.
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