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Group 15 Elements in Organic Synthesis : Reactivity of *tris*(dimethylamino)phosphane and stibane on Pyrylium Salts

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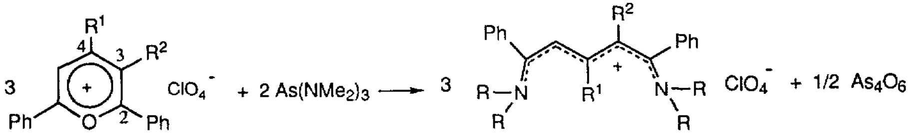
ABSTRACT : *The reaction of tris-dialkylaminoarsanes on pyrylium salts, giving a new series of pentamethinium salts was extended to the stibanes homologs whereas tris-dimethylaminophosphane yields only phosphonium adducts on the same substrates.*

We have recently discovered a new reaction of *tris*(dialkylamino)arsanes on pyrylium salts, leading to originally substituted pentamethinium salts[1].



eq. 1

An important question arises on the specificity of the organoarsenicals in this reaction specially towards phosphorous compounds and the aim of this article is to answer this question.

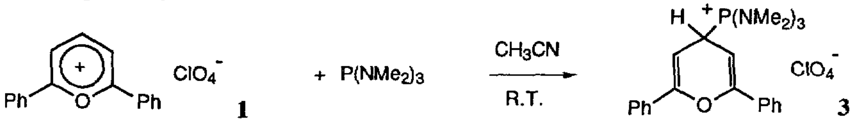
In the literature, there are some striking examples of group 15 compounds reactions on pyrylium salts[2]. Among them is the ammonia addition leading to pyridines and the Märkl's phosphabenzene synthesis[3]. Besides the addition of the arsenical homologs (i.e. AsH_3) was unsuccesful. The electrophilicity of the C-2 carbon of the pyrylium ring is not sufficient to lead to arsabenzenes. This fact is emphasized by the Märkl's work on azapyrylium salts where the cyclic nitrogen atom enhances the C-2 positive charge[4] to yield azaarsimines. An analogous reaction was recently developed with diazacompounds in phosphorus series[5].

Finally, the X-Ray structure of the adduct of $P(Ph)_3$ on 2-6 diphenyl pyrylium perchlorate was recently described[6] giving a phosphonium intermediate on the ring C-4 position. Other examples of phosphorus compounds addition are known[7] leading to neutral C-4 phosphonate species.

We describe here the results obtained with *tris*(dimethylamino)phosphane and stibane. The addition of $P(NMe_2)_3$ was attempted on two different pyrylium salts, the 2,6-diphenyl pyrylium **1** and the 2,4,6-triphenyl pyrylium **2** perchlorates. The latter compound presents a sterically hindered C-4 position. All experiments are made with acetonitrile as solvent.

In the case of the reaction of **1** with $P(NMe_2)_3$ a variation of the **1**/$P(NMe_2)_3$ ratio clearly demonstrates that the real reaction one is :

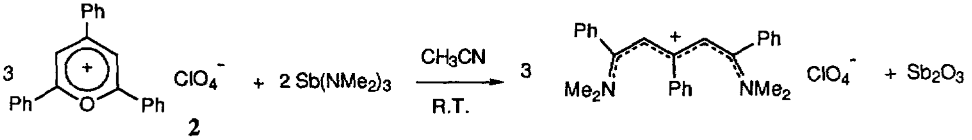
In the case of the reaction of **1** with $P(NMe_2)_3$, starting from the stoechiometric coefficients of eq. 1 (i.e. 3 and 2 respectively) a variation of the **1**/$P(NMe_2)_3$ ratio clearly demonstrates that the real reaction one is :



eq. 2

The ^{31}P NMR spectrum of **3** in CD_3CN presents a unique phosphonium signal at 53.16 ppm. The product **3** was also isolated and all physical data and elemental analysis are in accordance with this structure [8]. In the case of **2** the same final result is obtained but the reaction slows down considerably due to the steric hindrance. Thus, under the conditions of eq. 2 we observe in ^{31}P NMR the progressive disparition of the $P(NMe_2)_3$ signal (~ 123 ppm) and the formation of an intermediate at 78.67 ppm. This intermediate tentatively assigned to the covalent phosphane adduct, disappears slowly with the formation of the 2,4,6-triphenylphosphonium perchlorate [9]. The reaction is complete only after 48 h at R.T.

In contrast, the *tris*(dimethylamino)stibane reaction course is similar to eq. 1 scheme leading to the pentamethinium salt :



eq. 3

The reaction, performed with a slight excess of $Sb(NMe_2)_3$ is complete in few minutes (~ 5) with a quantitative yield. The final product is characterized as in [1] demonstrating that in one hand reactions of eq. 1 or eq. 3 are equivalent and in an other hand that the pyrylium salt transformation can also be achieved with other group 15 elements under the arsenic row. This fact is also emphasized by the reactivity of $As(NMe_2)_3$ and $Sb(NMe_2)_3$ towards carbonyl compounds giving enamines in each cases. The mechanism of these reactions should be the same, begining by a nitrogen attack on the carbon (δ+) of the carbonyl group [10]. A closely related mechanism is to consider for the primary attack of *tris* (dialkylamino)arsanes or stibanes on the C-2 of the pyrylium salt. Nevertheless for synthetic purposes, it seems better to use arsenia instead of stiba compounds for the access to this latter series is more difficult. The synthesis of $Sb(NR_2)_3$ necessitates aminolithium intermediates [11] and they are less stable. Moreover though Sb_2O_3 is a good leaving group it precipitates under voluminous flocky form difficult to filter or elutriate.

References and notes

1. Madaule, Y.; Ramarohetra, M.; Wolf, J.G.; Declercq, J.P.; Dubourg, A. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 994-6.
2. For a recent review, see Balaban,A.T. *Org. Synth. Mod. Trends*, Proc.IUPAC, Symp. 1986 (Pub. 1987), 263-274.
3. Märkl, G.; Lieb, F.; Merz, A. *Angew. Chem. Int. Ed. Eng.* **1967**, 6, 458.
4. Märkl, G.; Dielt,S. *Tetrahedron Lett.* **1988**, 29, 535-538.
5. Märkl, G.; C. Dorges,C. *Angew Chem. Int. Ed. Eng.* **1991**, 30, 106-7.
6. Abaev, V.T.; Kirasova, L.I.; Emarmilidi, S.E.; Bumber, A.A.; Mikhailov, I.E.; Blank, I.V.; Yanovskii, A.I.; Strüchkov, Yu T. ; Okhlobystin, O. Yu *Zh. Obshch. Khim.* **1989**, 59, 1506-15.
7. Chen, C.H; Reynolds, G.A. *J. Org. Chem.* **1980**, 45, 2449-53.
8. **3** : yield : 96% ; MP = 148°C, white powder recrystallized from absolute EtOH. Elemental analysis Calc., found : C (55.70; 55.83) ; H (6.30 ; 6.33) ; N (8.47 ; 8.47) ; O (16.13 ; 15.70) ; P (6.25 ; 6.40) ; Cl (7.15 ; 7.30). NMR (CD_3CN) : ^1H : δ (NMe_2), 2.79 ppm $^3J_{P\text{-}H}$ = 9.60 Hz. System AB_2X (X = P) ν_A = 4.63 ppm , ν_B = 5.29 ppm ; J_{AB} = 5.10 Hz, J_{AX} = 13.05 Hz , J_{BX} = 3.05 Hz ; ^{13}C (δ NMe 37.57 ppm, $^2J_{P\text{-}C}$ = 2 Hz) ; (δ C-4 33.06 ppm, $^1J_{P\text{-}C}$ = 105.4) ; (δ C-3 90,65 ppm, $^2J_{P\text{-}C}$ = 8.5 Hz) ; (δ C-2 154.32 ppm, $^3J_{P\text{-}C}$ = 9.7 Hz) ; ^{31}P : δ = 53.15 ppm.
9. NMR (CD_3CN) : ^{31}P : δ = 51.30 ppm; ^{13}C (δ NMe 38.01 ppm); (δ C-4 36.38 ppm ; $^1J_{P\text{-}C}$= 46.9 Hz)
10. a - Arsanes :Manoussakis, G. *J. Inorg. nucl. Chem.* **1968**, 30, 3100-03.; Anderson, R.H.; Cragg, R.H. *Inorg. Nucl. Chem. Letters* **1971**, 7, 583-5.; b - Stibanes :Kiennemann, A.; Kieffer, R. *J. Organometal. Chem.* **1973**, 60, 255-70.
11. Kiennemann, A.; Levy, G.; Schué, F.; Tanielan, C. *J. Organometal. Chem.* **1972**, 35, 143-8.

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