Arsacymantrenes: Direct Synthesis and Acetylation

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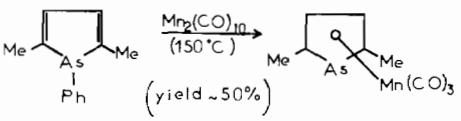
Recently, Abel *et al.* [1] prepared tetraphenylarsacymantrene by the pyrolysis of tetraphenylarsolepentacarbonyl manganese. The authors however do not give any details on the preparation of this σ complex.

Following our previous works on phosphacymantrenes [2], it seemed interesting to attempt the preparation of arsacymantrenes via a more direct route and to investigate electrophilic substitution reactions on the protons of the arsolyl cycle as we did for the phospholyl one.

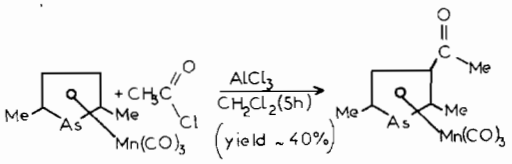
After Lambert's works [3], describing the As–Ph bond cleavage by $Mn_2(CO)_{10}$ in boiling xylene and after our works on phosphacymantrenes, we studied the reaction of the 1-phenyl 2,5-dimethylarsole (which was prepared according to Markl's method [4]) with $Mn_2(CO)_{10}$ in boiling xylene. After addition of an equimolar amount of the reagents, the reaction mixture was heated for 4 hours under argon, filtered, the filtrate evaporated to dryness and the residue chromatographed with pentane on a silical gel column. This yielded 2,5-dimethylarsacymantrene in one step as yellow crystals (M.p. ~40 °C).



This compound was characterized as follows: *Anal.* Found: C, 36.73; H, 2.79; calc. for $C_9H_8A_sMnO_3$: C, 36.76; H, 2.74%; ^{1}H NMR (in $CDCl_3$, TMS): δ, 1.91 (s, 6H; Me); 5,40 (s, 2H; CH); ^{13}NMR; δ, 18,3 (Me); 93,5 (C_β); 128,4 (C_α); 224.2 (CO); IR (hexadecane): νCO, 2020, 1948, 1942 cm^{-1} and mass spectrum (70 eV) m/e (I %): 294 (M, 30); 266 (M – CO, 8); 238 (M – 2CO, 30); 210 (M – 3CO, 100); 155 ($C_6H_8A_s$,6); 55 (Mn, 76).

According to the IR and ^{13}C NMR data, the arsolyl cycle seems a better electron donor ligand towards the $Mn(CO)_3$ rest than its phosphorus homologues.

2,5-dimethylarsacymantrene reacts in boiling methylene chloride with the CH_3COCl–$AlCl_3$ complex to yield the monoacetylated compound in β position:



The acetylated compound is purified by chromatography on silica gel (eluent:benzene), yielding an orange solid (m.p. ≅50 °C). It was characterized in the same way: *Anal.* Found: C, 40.19; H, 3.21; calc. for $C_{11}H_{10}A_sM_nO_4$: C, 39.31; H, 3.00%; ^{1}H NMR (in $CDCl_3$, TMS): δ 1,93 (s, 3H, Me-C_5); 2,24 (s, 3H, MeCO); 2,54 (s, 3H, Me–C_2) 6,02 (s, 1H, CH); IR (hexadecane): νCO, 2025, 1959, 1692 cm^{-1} and mass spectrum (70 eV) m/e (I %): 336 (M, 21); 308 (M – CO, 1); 280 (M – 2CO, 21); 252 (M – 3CO, 100); 224 (M – 4CO, 8); 169 ($C_7H_{10}A_s$, 3); 55 (Mn, 26).

Therefore arsacymantrenes are the first heterocycles including one arsenic atom, which have a real aromatic chemistry: thus these compounds can be acetylated even when the α position (which seems at first the best) is already occupied. This result was not obvious because, if phosphacymantrenes are so acetylated without decomplexing, on the contrary azacymantrenes are acetylated with decomplexation of the pyrolyl cycle [5]. Moreover, phosphacymantrenes are acetylated only when a methyl group is present in β position.

References

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