

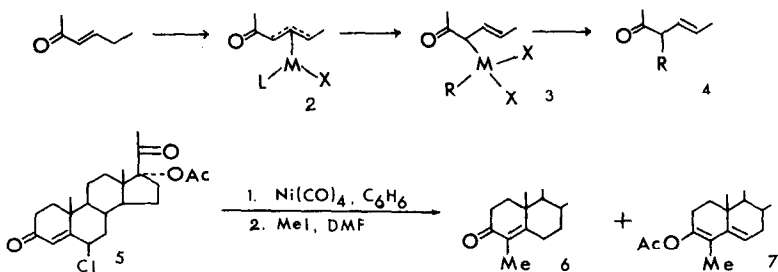
ALKYLATION OF ENONES VIA  $\pi$ -ALLYL COMPLEXES

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A recent publication<sup>1</sup> describing the preparation and reactions of  $\text{PdCl}_2$   $\pi$ -allyl complexes of steroids prompts us to present our work in this field. The potential utility of  $\pi$ -allyl complexes as reactive intermediates for the alkylations of enones, under mild non-basic conditions, is suggested by the known coupling of  $\pi$ -allyl  $\text{NiBr}_2$  with alkyl halides.<sup>2</sup> Thus reaction of the complex 2 with alkyl halides would be expected to furnish the alkylated enone 4, conceivably by way of an intermediate  $\sigma$ -complex 3.<sup>2</sup>

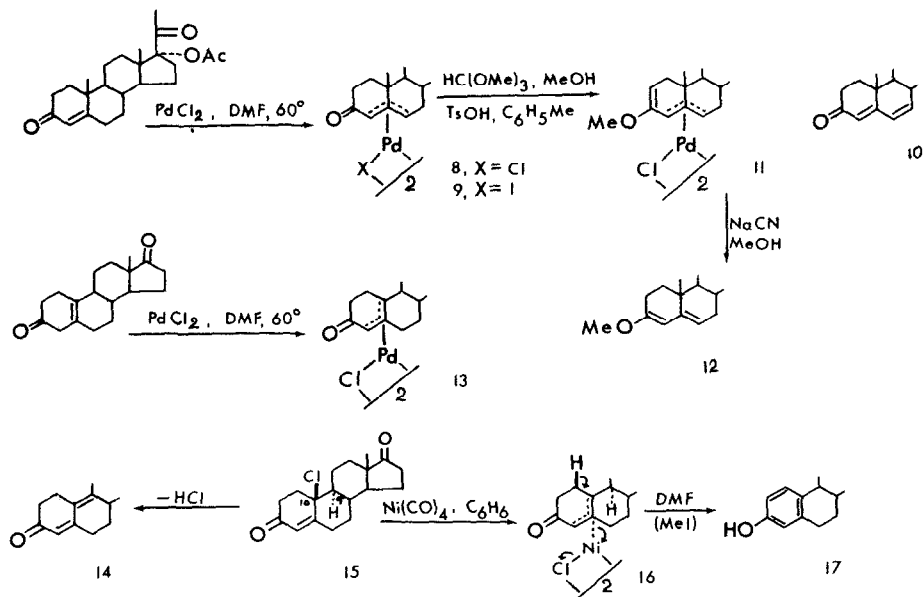


Treatment of the enone 5 with nickel carbonyl gave a red complex which reacted with methyl iodide forming the 4-alkylated derivatives 6 and 7 in about 24% combined yield. The enol acetate 7 presumably arises from a reaction of the steroid with acetyl iodide, a carbonylation product of methyl iodide.

Palladium chloride  $\pi$ -allyl complexes on the other hand are less reactive than their nickel analogs. Predictably, the complex 8 was not alkylated by methyl iodide although the previously noted halogen exchange,<sup>1</sup> forming the palladium iodide complex 9, was observed. Reaction of the complex 8 with the strong nucleophiles cyanide and malonate ion led to the elimination product 10. On treatment with methyl orthoformate 8 gave the enol ether 11 which was reduced to 12 by sodium cyanide in methanol. The novel  $\text{PdCl}_2$  complexes 8, 11 and 13 were prepared directly from the steroid by heating with  $\text{PdCl}_2$  in DMF.<sup>3</sup>

Attempted alkylation of the  $\text{NiCl}_2$   $\pi$ -complex 16 gave a good yield of estrone

17. It has been shown<sup>4</sup> that base treatment of 10-chloro-enones similar to 15 normally leads to the dienone 14 by a trans-elimination of HCl. The formation of estrone in our case suggests the  $\alpha$ -stereochemistry of the NiCl<sub>2</sub> moiety in 16 which would be trans with respect to the  $\beta$ -hydrogen on C-1.



Complex	$[\alpha]_D$	$\lambda$ max (e) (m $\mu$ )	$\delta$ vinyl 2-H	protons (ppm) 4-H	6-H
8	+260° (diox.)			3.43(s)	4.38(m)
9	+183° (chl.)	278 (16,100) (meth.)		3.52(s)	4.60(m)
11	-632° (diox.)		5.07(m)	3.65(s)	4.09(d)
13	+226° (chl.)	280 (11,000) (chl.)		4.76(s)	

## REFERENCES

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