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ON THE MECHANISM OF ALLYLIC ALKYLATIONS CATALYZED BY PALLADIUM

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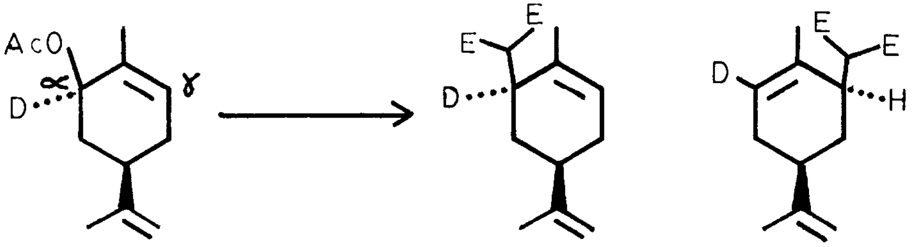
ABSTRACT: Results are reported indicating the intermediacy of a symmetrical π-allyl species in the alkylation of an allylic lactone. A previous report indicating that another mechanism was operative is disputed.

The ability of Pd(0) to catalyze allylic displacements by nucleophiles frequently provides complementary selectivity to standard methods of alkylation.[1] While attention has focussed heavily on the synthetic aspects, a mechanistic rationale invoking a functional equivalent of a π-allylpalladium cationic complex has been forwarded as best in accord with experimental observations.[2,3] Recently, this rationale has been questioned upon deuterium labelling studies and optical induction studies.[4] In the alkylation of 1, an α to γ alkylation ratio of 1.04 was reported. Considering that this ratio corresponds to a 51:49 mixture and the analytical method involved in NMR spectroscopy, this result appears to be best in accord with our interpretation. On the other hand, the optical rotations reported are difficult to understand on the basis of any mechanism. Several years ago, we had carried out a related study using optical activity as a mechanistic probe. Because of the uncertainties raised by the recent Tetrahedron Letters publication, we wish to report our observations at this time.

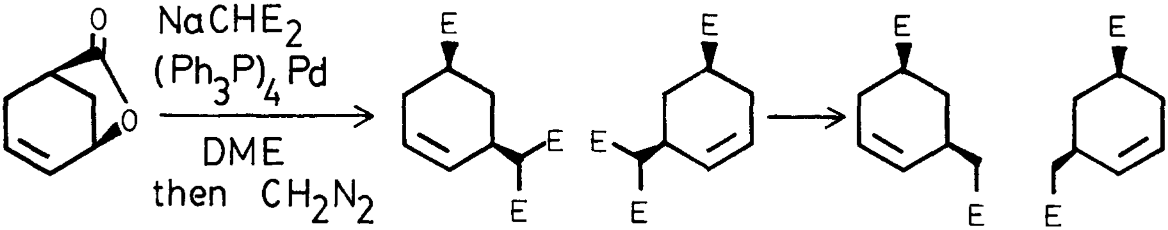


1

51%

49%

Alkylation of optically active lactone 2[5] ($[\alpha]_D$ = -66.2 [c=3.00, $CHCl_3$], 39% optically pure) with dimethyl sodiomalonate catalyzed by 4 mol% tetrakis(triphenylphosphine)palladium in the presence of 8 mol% triphenylphosphine in DME at reflux led to triester 3 in 75% yield after esterification with diazomethane. No optical rotation at either 589 nm or 578 nm was observed using a neat sample of 3 - a fact which suggested the product was racemic. To verify this result, we effected decarbomethoxylation of 3 [KOAc, DMSO, 115°]



2 3a 3b 4a 4b

to give 4 which showed an observed rotation of +0.042° at 589 nm and +0.049° (c=74.8, CCl_4) at 578 nm which corresponds to $[\alpha]_D$ = +0.056°. This value corresponds to 1.6% retained optical activity[6] after correction for the optical purity of the starting material. Within a reasonable allowance for experimental error, these results correspond to the product being racemic. Further support for the racemic nature of this product comes from a chiral shift study using 13 mol% $Eu(hfbc)_3$[7] where the quartet for the C-4 axial proton, originally at δ1.31 (J=12 Hz), splits into two quartets ($\Delta\delta$ = 0.78) of equal intensity.

These observations confirm the deuterium labelling results and are best in accord with our original interpretation. We wish to emphasize that our interpretation is based upon an intermediate that has an effective symmetry corresponding to a π-allylpalladium cationic complex. For example, rapidly interconverting σ-complexes also adequately rationalize the results. Considering that palladium complexes seem to prefer the π-allyl form, we currently favor the π-allylpalladium cationic intermediates,[8] although the question remains to be fully resolved.

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