can participate in these modes of rearrangement. In the event when **3** was treated with potassium hydride in tetrahydrofuran at reflux, *no* reaction was apparent. Addition of dicyclohexyl-18-crown-6 to the above system caused a clean transformation of **3** into the enol ether **7:** ν_{max} 1664 cm^{-1}. Mild acid hydrolysis of **7** gave the spirodihydrofuran-3(2*H*)-one **11:** ν_{max} 1750 cm^{-1}; τ 8.48 (4 H, m), 8.06 (2 H, m), 7.58 (2 H, t, J = 8 Hz), 5.96 (2 H, t, J = 8 Hz), 4.73 (1 H, d, J = 11 Hz), 4.08 (1 H, m). It should be noted that we were unable to detect any products resulting from competitive [3,3]- or [1,3]-sigmatropic processes. It may well be that the [3.3]-sigmatropic process is precluded because the conformation of the cyclohexene ring does not allow good overlap of the orbitals required in the transition state leading to a [3.3] process.

Both cyclopentanone and cyclohexanone gave the adducts **4** (n = 2 and 3, respectively) when treated with **2**. Adduct **4** (n = 2) required 4 days in THF–KH–dicyclohexyl-18-crown-6 at reflux to accomplish the conversion into **8** (n = 2), while adduct **4** (n = 3) required only 12 h. The rate of the above reactions was considerably increased (to ~2 h) by conducting the cyclization in *t*-BuOH–*t*-BuOK–dicyclohexyl-18-crown-6 at reflux. Acid hydrolysis of **8** (n = 2 and 3) furnished the dihydrofuran-3(2*H*)-ones **12** (n = 2 and 3, respectively). A particularly interesting example of this new cyclization reaction is the conversion of 3-methoxyandrost-3,5-dien-17-one into the new class of 17-spiro steroid derivatives **13**,[6] in an overall yield of 47%. Estrone was converted through the same sequence into **14**, 57%.

In orbital terms a clear explanation is evident. The terminal π orbitals of the allene are orthogonal to the π orbitals of the enol ether portion of the allene system; consequently the developing negative charge at the central digonal carbon atom occurs in an orbital that is in the same plane as the methoxyl group, the required geometrical situation.[7]

Dihydrofuran-3(2*H*)-ones, while a comparatively simple functional array, are a somewhat rare class of compounds.[8] The muscarine alkaloids are virtually the only class of natural products that contain the dihydrofuran-3(2*H*)-one moiety.[9] The route described here offers the only method, at present, for converting a carbonyl group into a spiroannulated dihydrofuran-3(2*H*)-one. The examples on 17-keto steroids provide a unique functional array at 17 which has in itself further possibilities of elaboration.[10] From the point of view of carbohydrate synthesis, it is viable to view dihydrofuran-3(2*H*)-ones as deoxy sugars with the view to introducing functional groups at positions α and β to the carbonyl group.

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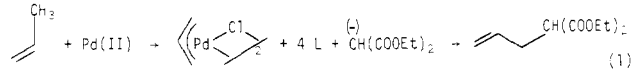
Palladium Catalyzed Allylic Alkylation of Olefins

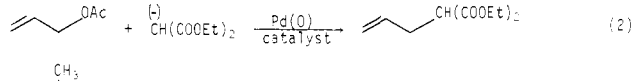
Sir:

Although allylic alkylation of π-allylpalladium halide complexes by stabilized carbanions in the presence of added ligands had been reported as early as 1965,[1] it has only been in the last few years that the process has been developed as a useful tool for organic synthesis.[2-15] The reaction can be carried out either stoichiometrically starting with an olefin and a Pd(II) complex (eq 1), or catalytically starting with allylic acetates and a Pd(0) complex (eq 2). In our studies of palla-

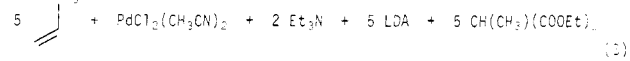


(1)

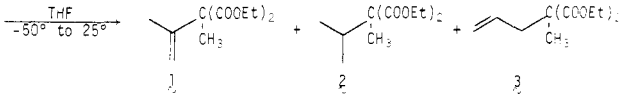
dium(II) assisted olefinic alkylations,[16] observations consistent with *direct catalytic allylic* alkylation of olefins were made and are summarized in eq 3. When olefin alkylation was car-



(2)



(3)



	1	2	3
5 h	90%	7%	0%
24 h	90%	7%	93%
42 h	90%	7%	180%

ried out using excess carbanion and excess amine, olefinic alkylation was complete and essentially quantitative after <4 h at 25 °C. On allowing the reaction mixture to stir for longer periods, *allylic* alkylation of the olefin was also observed. After 42 h there remained 97% olefinic alkylation products (**1, 2**) and 180% allylic alkylation product (**3**) (based on Pd), indicating that 2.8 mol of olefin reacted/mol of Pd. After 42 h, a considerable amount of metallic palladium was present, and no further reaction occurred. The same catalytic allylic alkylation of propene was observed using π-allylpalladium chloride as the palladium source. Thus treatment of 1 equiv of π-allylpalladium chloride with 10 equiv of triethylamine and then excess propene and $LiC(CH_3)(COOEt)_2$ (generated from

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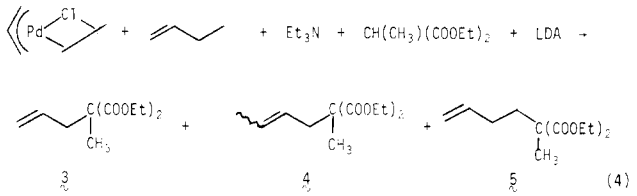
$CH(CH_3)(COOEt)_2$ and LDA at −60 °C) at −60 °C, followed by warming to and stirring at 25 °C for several days, resulted in the production of **3** in 262% yield by GC (196% isolated by preparative layer chromatography).[17] Repetition of this experiment led to GC yields of **3** ranging from 220 to 291%.

This reaction was not limited to propene. Carrying out the above experiment with π-allylpalladium chloride and excess 1-butene produced butenyl products **4** and **5**[18] (0.6:1) in overall 125% yield, as well as **3** (50%) from direct alkylation of the starting allyl complex (eq 4). Attack at the less substituted



(4)

position of butene predominated, as is usual for π-allylpalladium complexes. Pent-1-ene and hex-1-ene reacted similarly, giving mixtures of olefin isomers, although the reaction was slower and less efficient than with propene. Surprisingly, cyclopentene, cyclohexene, and allylbenzene failed to produce allylic alkylation products under these reaction conditions.

π-Allylpalladium chloride or $PdCl_2(CH_3CN)_2$ were the best sources of palladium for the above reactions. Use of $Pd(CH_3CN)_4(BF_4)_2$[19] or (π-allyl)$Pd(BF_4)$[20] produced only small amounts of allylic alkylation product. Since these reactions always produced a great deal of metallic palladium, and since it was difficult to devise a mechanism involving homogeneous complexes as catalysts, the possibility of heterogeneous catalysis was probed. The reaction described in eq 3 was rerun. After 6 h at 25 °C, the mixture, which contained large amounts of suspended metallic palladium, was centrifuged, and half of the clear supernatant was transferred to a degassed vessel, while the remainder of the liquid phase was left in contact with the palladium precipitate. Analysis of both fractions showed 94% **1**, 7% **2** and 21% **3**. After an additional 2 days at 25 °C, the transferred fraction remained clear (no Pd(0) precipitate) and contained 96% **1**, 8% **2** and 18% **3**, while the solution left in contact with the palladium precipitate analyzed for 98% **1**, 5% **2** and 98% **3**. That is, the homogeneous fraction produced no additional allylic alkylation product (**3**) after separation from metallic palladium, while the same solution left in contact with the precipitate produced an additional 80% **3**. This result is also reproducible and clearly implicates heterogeneous catalysis. Other heterogeneous Pd catalysts were checked for activity in this system, but they were all considerably less active. Thus 10% Pd on carbon, 5% Pd on silica gel, and 10% $PdCl_2$ on silica gel all catalyzed the reaction of propene with diethyl methylmalonate in the presence of triethylamine, but only ~20–25% yields of allylic alkylation product **3** (based on palladium) were obtained. Even smaller amounts (10–15%) of vinyl alkylation product **1** were obtained. Similarly, "Rieke Palladium"[21] was prepared by the reduction of $PdCl_2$ with potassium in the presence of 2 and 4 equiv of triethylamine. These complexes also produced **3** in only low yield. Finally, the homogeneous Pd(0) complex, bis(dibenzilideneacetato)-palladium,[22] gave only ~20% allylic alkylation. Thus the heterogeneous Pd generated by the reaction of $PdCl_2$ or π-allylpalladium chloride with stabilized carbanions and propene is a more efficient catalyst than the other types examined.

Although the mechanism of this catalytic allylic alkylation of olefins is not yet clear, the process is related to the palladium catalyzed amination of allyl alcohols and esters,[23] and alkylation of allyl ethers and esters by stabilized carbanions[2-15,23,24] or enamines,[25] all of which are thought to proceed via π-allylpalladium complex intermediates produced by Pd insertion into the allylic carbon–heteroatom bond. The reaction reported in this communication must involve insertion of palladium into an allylic C–H bond to produce a π-allylpalladium hydride, which reacts further to form the observed products. This process is similar to that observed with $(CH_3CH{=}CH_2)NiPF_3$, which is in equilibrium with (π-allyl)$Ni(H)PF_3$ at low temperatures.[26] Studies are in progress to elucidate the mechanism and to extend the lifetime and increase the rate of this allylic alkylation of olefins.

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Bis Heteroannulation. 1. Model Studies in the Synthesis of Highly Oxygenated Sesquiterpenes

Sir:

The uncovering of significant biological activity in certain highly oxygenated members of the sesquiterpene class has been greeted with an enormous outpouring of effort directed toward either the partial, or total, synthesis of representative compounds.[1] We, too, have recently been attracted to this area, but, while the structural diversity of these materials is renowned (cf. Chart I), we have chosen in our own efforts to focus on a number of subtle features which are apparently held in common. Namely, (1) they either contain a furan ring *or* a functionality *in principle* derivable from a furan ring; (2) the more biologically active compounds usually contain an oxygen functionality adjacent to the furan or lactone ring juncture;[2] and (3) most of the stereochemically interesting features are contained about the periphery of a single ring. These points,

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