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ON THE QUESTION OF CARBONIUM ION INTERMEDIATES IN THE PALLADIUM (II) CHLORIDE-COPPER (II) CHLORIDE CATALYZED ADDITION REACTIONS OF BYCYCLIC OLEFINS

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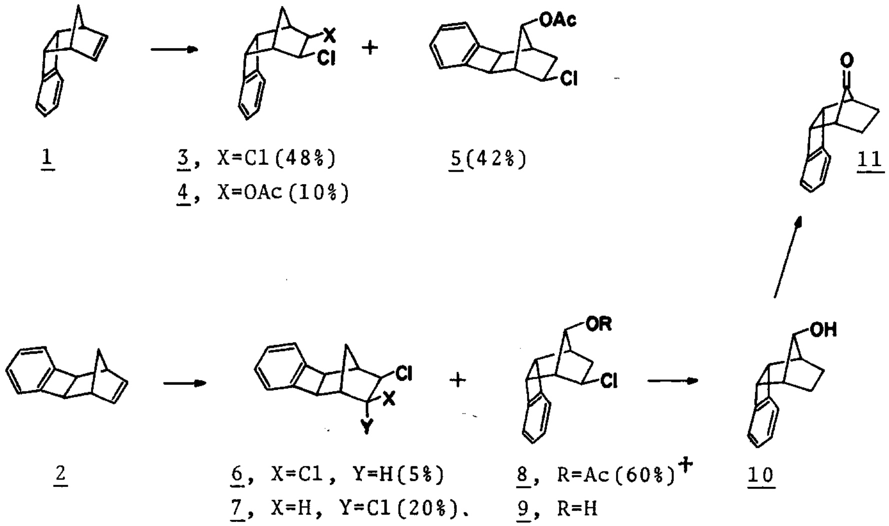
In a recent communication the palladium (II) chloride catalyzed addition reactions of olefins 1 and 2, in the presence of $CuCl_2$/AcONa-AcOH, were described.[1] Additional investigations have provided a different conclusion regarding the stereochemistry of an important product, which now prompts us to report an unusual rearrangement in the reaction involving 2. Although one of the interests in these studies stemmed from the opportunities offered in the synthesis of a series of tricyclo[$4.2.1.0^{2,5}$] non-9-yl derivatives,[2] it has become evident that the data provides useful mechanistic details of the reaction of palladium chloride with bicyclic olefins.

Treatment of endo-olefin 1 with $PdCl_2$-$CuCl_2$/HOAc, according to the accepted procedure,[3] afforded a crude product mixture which showed two acetate methyl signals in the n.m.r. at τ 7.98 and 8.02. Column chromatography (neutral alumina) using hexane, hexane/ether (1:1) as eluants afforded dichloride 3 and chloroacetates 4 and 5 (Scheme 1).[1] The structure of chloroacetate 4 (not detected in the previous[1] investigation) was assigned on the basis of n.m.r. and mass spectral data; m.p. 136-138°, n.m.r. ($CDCl_3$), τ2.82 (m, 4H), 5.62 (dd, 1H, J=6.0, 1.8 Hz), 6.30 (m, 3H), 7.28 (m, 2H), 7.63 (complex d, 1H, J=10.5Hz), 7.98 (s, 3H), 8.32 (complex d, 1H, J=10.5 Hz); mass spectrum (70eV) m/e (rel. intensity), 264 (1), 262 (3), 227 (11), 202 (25), 167 (33), 155 (13), 142 (72), 141 (26), 129 (30), 128 (11), 115 (11), 91 (23), 77 (22), 43 (100).[4] Whereas the mass spectrum of 5 shows a ratio of M^+-60 ion (loss of acetic acid) to parent ion (M^+) of 0.6, the corresponding ratio for 4 was 8.3.

Scheme 1. $PdCl_2$-$CuCl_2$ Addition Reactions in AcOH-AcONa



1

3, X=Cl(48%)
4, X=OAc(10%)

5(42%)

11

2

6, X=Cl, Y=H(5%)
7, X=H, Y=Cl(20%).

8, R=Ac(60%)†
9, R=H

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The product mixture from similar treatment of exo-olefin 2 was readily separated by chromatography on neutral alumina to give dichlorides 6 and 7 and the chloroacetate 8 (m.p. 89-90°), whose previously assigned[1] stereochemistry has been reconsidered on the basis of the following data. The mass spectrum of 8 revealed an M^+-60 ion which was less intense than the parent ion, thus implying in contrast with 4, that the acetoxy function is in the bridge postion. While the 60 MHz spectrum ($CDCl_3$) [τ2.88 (m, 4H), 5.13 (br. s, 1H), 6.20-6.60 (m, 3H), 7.05 (br. d, 1H, J=5.0 Hz), 7.29 (br. t, 1H, J=5.0 Hz), 7.94 (s, 3H), 8.00-8.50 (m, 2H)], was consistent with, but not definitive for structure 8 the 100 MHz spectrum of the derived chlorohydrin 9, taken in benzene, confirmed the suggested structure beyond reasonable doubt. Most significantly, the benzylic protons (quintet) in the latter spectrum appeared well separated from the C_7, α-Cl

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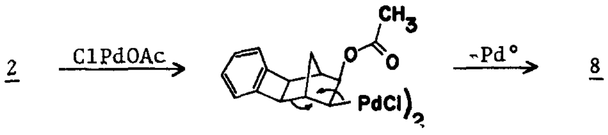
† A further product (ca. 15%) could not be obtained in sufficient purity for structural assignment.

proton which consisted of a large doublet of doublets (coupling with the two adjacent C_8 protons) with each line further split into a smaller doublet (J=1.3 Hz) from long range coupling with the C_9 proton. Chemical proof for structure 8 and 9 was obtained by sodium/liquid ammonia/ethanol reduction[5] to the known[6] alcohol 10 (m.p. and m.m.p. 109-110°), followed by oxidation by CrO_3/pyridine to the known ketone 11.

The assignment of structure 8 to the chloroacetate from *exo*-olefin 2 prompted a reassessment of the problem since by any of the previously suggested mechanisms[1,3] this product from 2 is difficult to explain. Reactions in which $PdCl_2$ was totally excluded, revealed that $CuCl_2$ alone could predominatly account for the unrearranged products. Thus, *endo*-olefin 1 under these conditions yielded *cis*-dichloride 3 (69.5%) and *cis*-chloracetate 4 (30.5%), while *exo*-olefin 2 gave *cis*-dichloride 6 (37.6%) and *trans*-dichloride 7 (62.4%).[7]

Products from the mixed $CuCl_2$-$PdCl_2$ reaction apparently arise from competitive reactions, probably involving at least two different metal-olefin complexes. A copper (I or II) complex with olefins 1 and 2 appears to be the controlling intermediate leading to unrearranged products, whereas the corresponding palladium (II) complexes lead to predominatly rearranged chloroacetates (under influence of copper (II) chloride[8]). It is apparent that neither of these competing processes proceed *via* free carbonium ion intermediates, for $CuCl_2$ with *endo*-olefin 1 yields only unrearranged products, whereas the intervention of free carbonium ions in this system has previously been demonstrated to lead to rearranged products exclusively.[9] Similarly, if free carbonium ions are involved in the reaction of *exo*-olefin 2 with $PdCl_2$, non-rearranged chloroacetate should obtain.[9] The isolation of rearranged chloroacetate 8 as the major product from 2 argues against this possibility.

One attractive explanation for the formation of 8 involves rearrangement of intermediate 12 *via* a 1,2-shift[8] of the appropriate C-C bond synchronous with capture of Cl^- and extrusion of Pd metal. Further experiments are needed to test this and other mechanistic possibilities in this area.



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