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PALLADIUM-CATALYZED DECARBONYLATION OF TRICYCLIC BRIDGEHEAD ACID CHLORIDES

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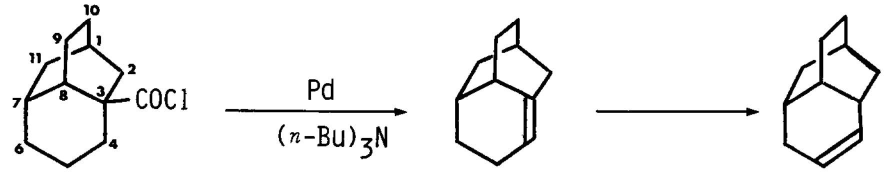
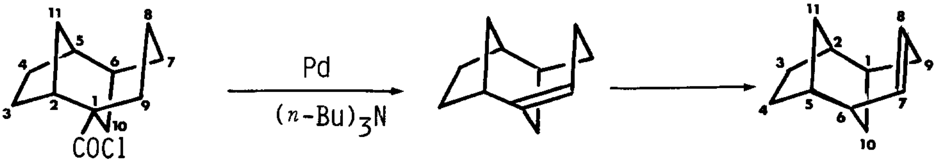
Summary: Decarbonylation of tricyclic bridgehead acid chlorides 1 and 4 with palladium catalyst in the presence of tri-n-butylamine proceeded at 130 °C to give exclusively stable disubstituted olefins 3 and 6, with probable intermediacy of the bridgehead olefins 2 and 5, respectively.

The chemistry of the strained bridgehead olefins, so-called anti-Bredt olefins, has extensively been studied in recent years from the structural and synthetic interests, and a series of elimination reactions have been developed for preparing bridgehead olefins.[1] Increasing attention has been paid on the stabilization of bridgehead olefins with transition metals.[2] In this paper, we wish to report the palladium-catalyzed decarbonylation[3] of tricyclic bridgehead acid chlorides in the presence of tri-n-butylamine to afford thermodynamically stable olefins.



(1) (2) (3)

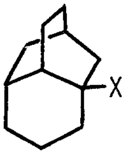


(4) (5) (6)

Previously, we have reported a ready formation of the bridgehead olefin, tricyclo[5.3.1.0^{3,8}]undec-2-ene (11) in dehydrobromination of 3-bromotricyclo-[5.3.1.0^{3,8}]undecane (8) with sodium amide.[4] As part of a continuing study of the chemistry of tricyclo[5.3.1.0^{3,8}]undecane (7),[5] we examined the decarbonylation reaction of 3-chlorocarbonyltricyclo[5.3.1.0^{3,8}]undecane (1)[5a] with palladium catalyst.

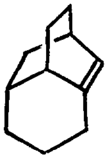
Treatment of the acid chloride 1 at 200 °C for 2 h with $PdBr_2$ (1 mol%) yielded a mixture of tricyclo[5.3.1.0^{3,8}]undec-4-ene (3)[6] and 3-chloro-tricyclo[5.3.1.0^{3,8}]undecane (9)[7] in 26 % and 58 % yields. Neither isomeric acid chloride[3d] nor carbon skeleton-rearranged olefin[8] was obtained under the reaction conditions.

However, addition of tri-n-butylamine (1.2 equiv to 1) in the above reaction changed the product distribution drastically, the olefin 3 being obtained exclusively. The reaction proceeded even at 130 °C, and a nearly quantitative yield of 3 was observed. Other palladium catalysts such as $PdCl_2$, $Pd(OAc)_2$ and $Pd(PPh_3)_4$ were also efficient for the reaction.

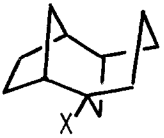


(7) X=H (9) X=Cl

(8) X=Br (10) X=OH



(11)



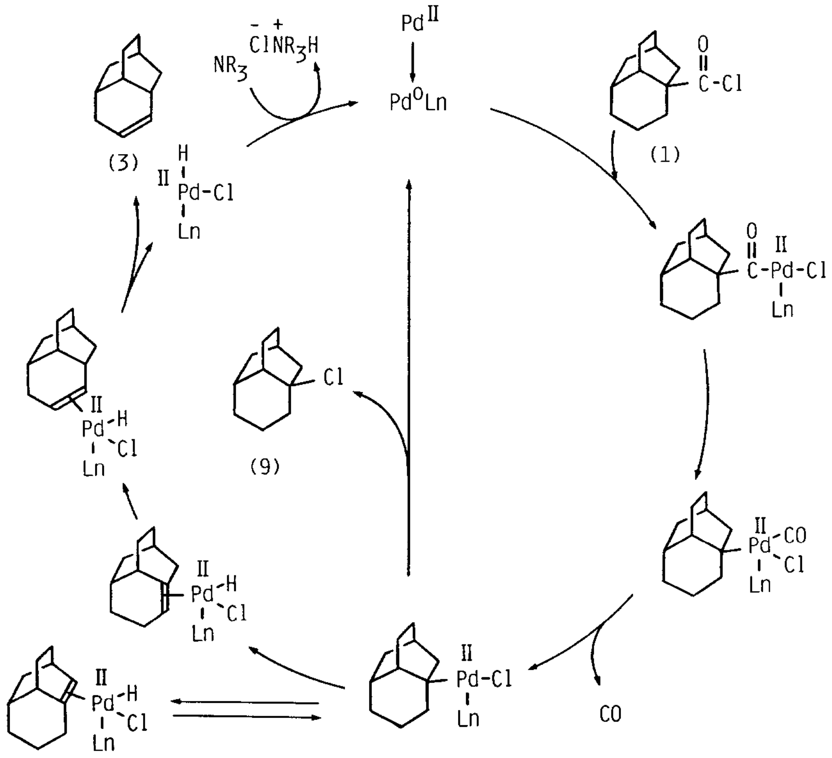
(12) X=H

(13) X=Br

(14) X=Cl

While the chloride 9 was stable under these reaction conditions, the bridgehead olefin 11 prepared aforehead isomerized to 3, with most probable intermediacy of another bridgehead olefin 3(4)-ene 2. In view of these findings and what is known for palladium-catalyzed decarbonylation of acyclic acid halides,[3a] a catalytic cycle as depicted in Scheme seems to a reasonable rationale for our reactions. Computation with the MM2 force field[9] shows that 3 ($\Delta H_f°$=-2.3 Kcal/mol) has a much greater stability relative to other isomers, 2 ($\Delta H_f°$=10.6 Kcal/mol) and 11 ($\Delta H_f°$=6.7 Kcal/mol). It might be assumed that tri-n-butylamine functions not only as a base but also as a ligand to affect on the selectivity and the rate of the reaction.

1-Chlorocarbonyltricyclo[4.3.1.1^{2,5}]undecane (4)[10] also gave the corresponding olefin, the 7-ene 6 ($\Delta H_f°$=1.7 Kcal/mol), exclusively in 84% yield.[11] The structure of 6 was elucidated on the basis of spectroscopic analysis as well as hydrogenation to tricyclo[4.3.1.1^{2,5}]undecane (12).[12] Similarly as for the reaction of 1, palladium-stabilized 1(9)-ene 5 ($\Delta H_f°$= 22.0 Kcal/mol)[13] might be proposed as a reaction intermediate.[2]



As the bridgehead acid chlorides are easily obtainable and since the reaction shows high selectivity for olefin formation under palladium-tertiary amine catalysis, this reaction is useful for the preparation of tricyclic olefins, which are usually difficult to be prepared. We are now examining the scope of this decarbonylation reaction on a variety of related cyclic acid chlorides.

References and Notes

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7. All new compounds gave satisfactory analytical and spectral data. Selective data are shown as follows. **9**: ^{13}C NMR (CDCl$_3$) δ 20.7 (t), 23.4 (t), 25.8 (t), 27.0 (d), 30.5 (t), 32.1 (t), 34.9 (d), 42.6 (d), 44.3 (t), 45.0 (t), 75.4 (s); MS (*m/z*) 186 (M$^+$, 2,), 184 (6), 149 (100), 148 (33), 107 (27), 81 (22). **14**: ^{13}C NMR (CDCl$_3$) δ 21.2 (t), 26.3 (t), 26.6 (t), 28.0 (t), 33.6 (t), 36.9 (d), 38.2 (t), 39.3 (d), 39.6 (t), 49.9 (d), 75.5 (s); MS (*m/z*) 186 (M$^+$, 4) 184 (9), 149 (100), 81 (32), 79 (34), 67 (88), 66 (25). **6**: ^{13}C NMR (CDCl$_3$) δ 27.4 (t), 28.7 (t), 29.0 (t), 31.2 (t), 33.2 (t), 33.5 (d), 35.7 (d), 38.1 (d), 42.6 (d), 129.5 (d), 132.8 (d); MS (*m/z*) 148 (M$^+$, 47), 119 (12), 80 (85), 79 (100), 78 (46), 67 (44).
8. Dehydration of 3-hydroxytricyclo[5.3.1.0^{3,8}]undecane (**10**) with a cation-exchange resin gave the structurally rearranged tricyclo[6.2.1.0^{2,6}]-undec-2(6)-ene as a main product: Takaishi, N.; Inamoto, Y.; Aigami, K.; *J. Org. Chem.* 1980, **45**, 2254.
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11. Without tri-*n*-butylamine, 1-chlorotricyclo[4.3.1.1^{2,5}]undecane (**14**, 37 %) was obtained along with the olefin **6** (61 %).
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13. In contrast to **8**, 3-bromotricyclo[4.3.1.1^{2,5}]undecane (**11**) did not give the bridgehead olefin **5** with sodium amide.

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