Palladium(II)-catalysed Rearrangement of Bicyclobutanes; Direct Observation of Intermediate Complexes

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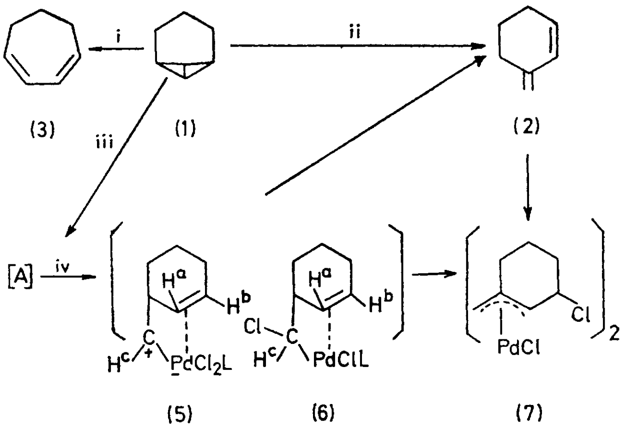
Summary The first spectral observation of intermediates in the transition metal-catalysed rearrangement of bicyclobutanes strongly supports the proposed intervention of an unstable carbene–palladium complex.

In the presence of catalytic amounts of transition metals a number of bicyclobutanes rearrange very readily to butadienes.[1] We have recently pointed out that the behaviour of Pd^{II} towards some bicyclobutanes is significantly different from that of Ag^{I}.[1b,2] Pd^{II} effects quantitative conversion of tricyclo[4,1,0,0^{2,7}]heptane (**1**) into 3-methylenecyclohexene (**2**); Ag^{I} catalysis produces exclusively cyclohepta-1,3-diene (**3**). Investigations on the structural relationship between various substituted bicyclobutanes and their rearranged products, and additional circumstantial evidence, has led us to propose that a Pd^{II}–carbene complex or its equivalent is probably involved in reactions catalysed by this metal.[2] We demonstrate that at least two discrete intermediates (including the one recently proposed) are involved in the skeletal transformation of bicyclobutanes.

Low-temperature n.m.r. studies are relevant to the rearrangement of (**1**). Thus, at −50° all the absorptions (in CD_2Cl_2) due to (**1**) virtually disappeared in the presence of $PdCl_2(PhCN)_2$ (**4**) (1·2 equiv.) and new, discrete signals appeared, indicating the formation of a complex or complexes (A).† These signals remained unchanged for at least 1 h at this temperature, but gradually disappeared at −30° and were finally replaced by another set of peaks: τ 4·42br (d, 1H, J 6·5 Hz), 4·73 (m, 1H), 6·21 (s, 1H), and 7·7—8·5 (m, 7H), apparently consistent with structure (**5**), corresponding exactly to the intermediates proposed previously.[2]

The first two signals are obviously at too low field for π-allylic protons and are assigned to H^a and H^b.[3] Structure (**5**), a formal carbene–metal complex, lacks precedents, except for stable methoxy-carbene complexes,[4] and assignment of H^c of (**5**) to the signal at τ 6·21 is reasonable. However, (**6**), an isomer of (**5**) also satisfies the spectral data and cannot be excluded.

After further warming of the same sample to 0° for 2 h or to 30° for 20 min, the n.m.r. spectrum showed peaks at τ 5·62br (s, 1H), 5·88br (s, 1H), 6·21br (s, 1H), 7·14br (s, 1H), 7·36 (m, 2H), and 7·6—8·5 (m, 4H). A 1:1 mixture of (**2**) and (**4**) reproduced this spectrum, so the π-allyl complex (**7**) is presumably present.[5] Treatment of this solution with pyridine, NH_3, or PPh_3 generated (**2**).



Scheme. *Reagents:* i, Ag^{I}; ii, Pd^{II} (*catalytic amount*), *room temp.*; iii, Pd^{II} (1·2 *equiv.*), −50°; iv, −15°.

(**7**) was formed very rapidly from (**2**) and (**4**), even at low temperatures. Treatment of (**1**) with (**4**) ($<$1 equiv.) produced (**2**) at −15°; (**5**) appears to be converted into (**7**) *via* (**2**). However, in the absence of detailed kinetic data, the direct route from (**5**) to (**7**) is not excluded.

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† Because of the complexity of this spectrum we have not been able to make a definite structural assignment.

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[2] M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Comm.*, 1971, 487.

[3] *E.g.*, E. Vedejs, *J. Amer. Chem. Soc.*, 1968, **90**, 4752.

[4] See series of publications by E. O. Fischer and his co-workers, *e.g.*, E. O. Fischer, B. Heckl, K. H. Dötz, and J. Müler, *J. Organometallic Chem.*, 1969, **16**P 29.

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