Palladium(II)-catalysed Ring Expansion of Methylenecyclobutanes and Related Systems

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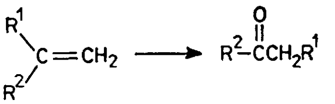
Summary Methylenecyclobutane and its 3-substituted derivatives undergo a palladium(II)-catalysed ring expansion to the corresponding cyclopentanones in good yield; camphene, methylenecamphor, and methylenecyclopentane undergo analogous but less efficient reactions.

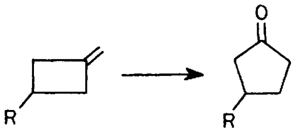
The palladium(II)-catalysed conversion of terminal olefins (**1**; $R^1 = H$) into methyl ketones (**2**; $R^1 = H$) by $PdCl_2$–$CuCl_2$–O_2–H_2O has been known for some time[1] and is analogous to the Wacker process.[2] We have recently described an intramolecular version of this process in which suitable vicinal dihydroxy terminal olefins are converted into cyclic acetals.[3] 1,1-Disubstituted olefins (**1**; R^1 and $R^2 \neq H$) are reported not to undergo conversion into ketones. However, we find that 1,1-disubstituted olefins can be rearranged to ketones in cases where migration of R^1 is specially favoured, *e.g.* when R^1 and R^2 are part of a strained ring or are phenyl groups.



$$R^1R^2C{=}CH_2 \longrightarrow R^2\overset{O}{\overset{\|}{C}}CH_2R^1$$

(1) (2)

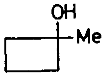
Thus methylenecyclobutane (**3**; R = H, 1 mol) gives cyclopentanone (**4**; R = H; 75%) with $PdCl_2$ (0·05 mol)–$CuCl_2$ (0·5 mol)–O_2–H_2O (2 mol) in benzene at 0 °C. Lower yields and mixtures result in other solvents, *e.g.* in ethyl acetate a mixture of (**4**), (**5**), and (**6**) (10 : 9 : 1) was obtained whilst in isopropyl alcohol the ratio of (**4**), (**5**), and (**6**) was 1 : 2 : 1. The substituted methylenecyclobutanes (**3**; R = CN) and (**3**; R = $CH_2HNCOMe$) undergo analogous ring expansions at 65 °C and room temperature, respectively, in ethyl acetate, giving (**4**; R = CN; 82%) and (**4**; R = CH_2-NHCOMe; 65%).



(3) (4)

$Cl[CH_2]_3COMe$

(5)



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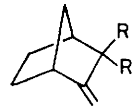

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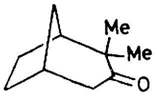

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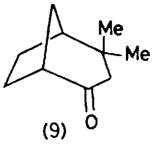

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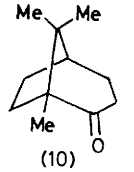

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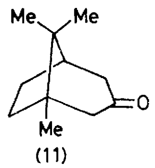

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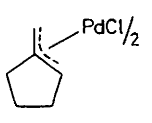

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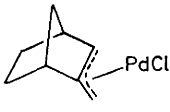

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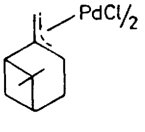
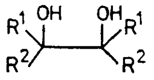


(14)

Ring expansion of camphene (**7**; R = Me) in isopropyl alcohol at 65 °C using the $PdCl_2$–$CuCl_2$–O_2–H_2O system gave a 3 : 1 mixture of the ring expanded ketones (**8**) and (**9**).[4] Methylenecamphor (ethyl acetate, 45 °C) gave a poor yield of two ring-expanded ketones (**10** and **11**; 3 : 1; *ca.* 20%)[5] together with unidentified by-products. Methylenecyclopentane (ethyl acetate, 65 °C) produced (20%) cyclohexanone in addition to the bis-π-allyl palladium chloride dimer (**12**; 95%). Methylenenorbornane (**7**; R = H) (Pr^iOH, 45 °C) and β-pinene (Bu^tOH, 45 °C) also gave essentially quantitative yields (based on $PdCl_2$) of the π-allyl complexes (**13**) and (**14**), respectively.[6]

The 1,1-diarylolefins (**1**; $R^1 = R^2 = Ph$) and (**1**; $R^1 =$ Ph, $R_2 = p\text{-}MeOC_6H_4$) have also been studied with the same catalyst system. Thus (**1**; $R^1 = R^2 = Ph$) (ethyl acetate, 65 °C, 25 atm of air) gave a 1:1 mixture of benzophenone (28·5%) and benzyl phenyl ketone (28·5%), together with unchanged starting material (32%), whilst (**1**; $R^1 = Ph$, $R^2 = p\text{-}MeOC_6H_4$) gave only phenyl *p*-methoxyphenyl ketone (62·5%). The oxidative cleavage of the olefinic double bond in these two cases presumably arises *via* the formation of the diol (**15**). Formation of chlorohydrin in the Wacker reaction is well documented[2,7] and we find that diols of type (**15**; $R^1 = Ar$, $R^2 = H$ or Ar) undergo oxidative cleavage to carbonyl compounds under the same conditions as those under which diaryl olefins give benzophenones.[8]



(15)

Methylene cyclo-olefins are capable of reacting with palladium chloride in a number of ways and, as our results illustrate, the preferred path is sensitive to olefin structure and solvent polarity.

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[3] N. Byrom, R. Grigg, and B. Kongkathip, *J.C.S. Chem. Comm.*, 1976, 217.

[4] Identical with samples prepared by the method of J. Wolinsky, *J. Org. Chem.*, 1961, **26**, 704.

[5] Identical with samples prepared by the methods of G. Quinbert, A. Moschel, and G. Buhr, *Chem. Ber.*, 1965, **98**, 2742; Y. Bessiere-Chretien and M. M. El Gaied, *Bull. Soc. chim. France*, 1971, 2189.

[6] This appears a less tedious and more efficient process for preparing bis-π-allyl palladium chloride dimers in these particular cases than those currently in use, *e.g.* B. M. Trost and P. E. Strege, *Tetrahedron Letters*, 1974, 2603.

[7] H. Stangl and R. Jira, *Tetrahedron Letters*, 1970, 3589.

[8] P. Boontanonda and R. Grigg, unpublished observations.