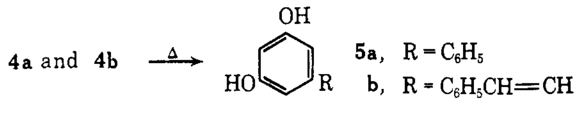
drying at a temperature sufficiently high to assure removal of this solvation. Acids **4a** and **4b** were decarboxylated; they afforded good yields of 5-phenylresorcinol (**5a**), mp 157–158° (reported[7] mp 157–158°), and pinosylvin (**5b**), mp 152–155° (reported[8] mp 156°), respectively. The melting points of resorcylic acids **4c–e** conformed satisfactorily to reported values. Only a small quantity of orsellinic acid (**4f**) was obtained, although the yield based on **1f** appeared to be good. Orsellinic acid was identified by thin layer chromatographic comparison with authentic material.[9]



The 6-alkyl-β-resorcylic acids **4c–f** are common metabolites of lichens and **4f**, the simplest of the series, is produced by fungi, as well.[3] Pinosylvin (**5b**) is found in the heartwood of pines, and is probably formed from **4b**.[2,3] The conversion of triketo acids **1** to resorcylic acids **4** in high yields under mild "physiological" conditions lends support to the postulate that triketo acids (or their esters) are precursors of such resorcylic acids in living systems. The ease with which these cyclizations occur in aqueous solutions tempts us to question whether they are of necessity effected enzymatically.

Variations in the cyclization conditions are currently being investigated to determine whether other equally mild conditions may lead to acylphloroglucinols or other aromatic condensation products.

---

(7) C. M. Suter and P. G. Smith, *J. Am. Chem. Soc.*, **61**, 166 (1939).

(8) H. Erdtman, *Ann.*, **539**, 116 (1939).

(9) The authentic sample was kindly furnished by Dr. R. J. Light, Florida State University.

**Thomas M. Harris, Robert L. Carney**
*Department of Chemistry, Vanderbilt University*
*Nashville, Tennessee*

*Received February 28, 1966*

---

## Allylic Oxidation of Olefins by Palladium Acetate[1]

*Sir:*

As reported recently,[2] allylic oxidation of certain 1- and 2-olefins by mercuric acetate in acetic acid involves SEi′ formation of allylic mercurials which rapidly equilibrate in favor of the primary isomer. This undergoes a unique SNi demercuration reaction leading to secondary allylic acetate, and thus pure secondary ester is obtained from either the 1- or 2-olefinic isomer. In this communication we report the contrasting allylic oxidation of olefins by palladium acetate.

The oxidation of olefins by $Pd^{II}$ salts under aqueous conditions to yield carbonyl compounds is well known,[3] and certain features of the mechanism have been recognized.[3,4] However, allylic oxidation of olefins by $Pd^{II}$ salts has received little attention, and the pathways to allylic products have been far from clear. Only in the case of cyclohexene has clean allylic oxidation been effected,[5] $\Delta^2$-cyclohexenyl acetate being essentially the sole product[6] from oxidation with $Pd(OAc)_2$ in AcOH. Further investigation, the results of which are now reported, shows that in olefin–$Pd(OAc)_2$ oxidation: (i) 1-olefins give mainly enol acetate while 2-olefins give mainly allylic acetate; (ii) 1-olefins and 2-olefins give different allylic acetates.

Oxidation of excess propene (Ia), 1-butene (Ib), *cis*- and *trans*-2-butene (IIb), 1-pentene (Ic), and *cis*-2-pentene (IIc) by $Pd(OAc)_2$ in AcOH proceeds smoothly at 25° to give high yields of monoacetate products. Any diacetates formed represent <2% of the product. From the 1-olefins, the predominant monoacetates are enol acetates, allylic acetate being a minor product. Thus, the monoacetate product from propene consists of 98.6% isopropenyl acetate[7d] (Va), *ca.* 0.5% *cis*- and *trans*-propenyl acetates[7c,8c] combined (VIa), and *ca.* 0.9% allyl acetate[7c] (VIIa). From 1-butene, the monoacetate product contains somewhat more allylic acetate, *ca.* 9% being observed. This material is purely primary (>99.5%), the crotyl acetate[7b] (VIIb) showing an 80:20 *trans*:*cis* ratio. The major product (*ca.* 80%) is the enol acetate[7a] Vb, other products being enol acetate[7c,8b] VIb (*ca.* 9%) and a material having the same vpc characteristics as 3-buten-1-yl acetate[8a] (*ca.* 2%). The product from 1-pentene contained *ca.* 10% of allylic acetate, >98% primary[7b] (VIIc), *ca.* 85% of an enol acetate[7a] Vc, and *ca.* 5% of two other materials with vpc behavior appropriate for enol acetates.

As in the case of cyclohexene,[5] oxidation of *cis*- or *trans*-2-butene leads nearly exclusively (>97%) to allylic acetate.[9] The latter is exclusively (>99.2%)

---

(1) (a) Research sponsored by the U. S. Army Research Office (Durham): (b) research supported in part by the National Science Foundation.

(2) Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Letters*, No. **42**, 3719 (1965).

(3) J. Smidt, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **1**, 80 (1962), and references there cited.

(4) P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964), and other included references; see the suggestion of J. Halpern quoted by R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p 88.

(5) C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).

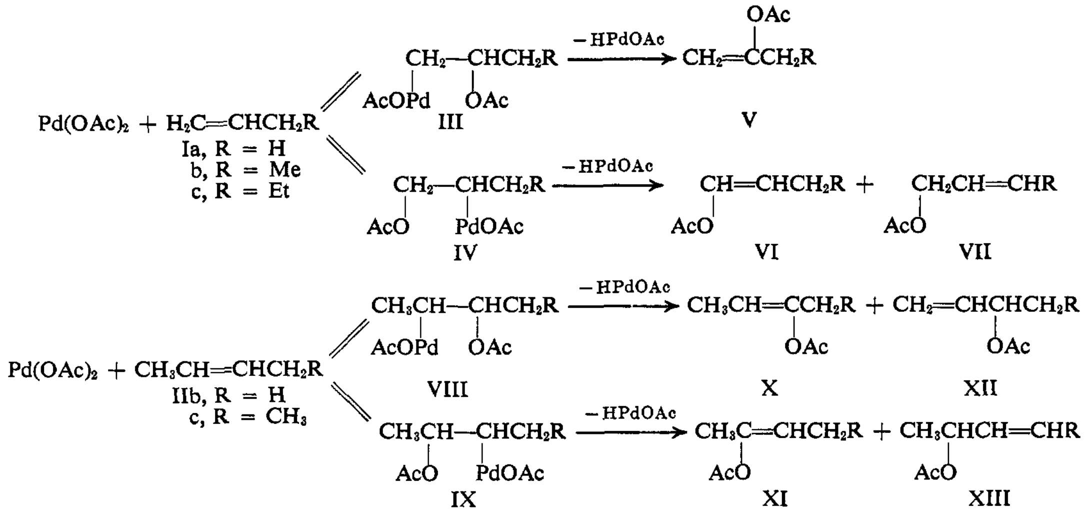
(6) Other reports of allylic oxidation have appeared. *E.g.*, see I. I. Moiseev, *et al.*, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960), and subsequent papers. These workers reported that oxidation of propene by $PdCl_2$ in AcOH yielded 15% allyl acetate. The $Pd(OAc)_2$–AcOH system is mechanistically simpler than $PdCl_2$–AcOH–NaOAc where questions of ligand competitions on Pd arise.

(7) (a) Identified by nmr and infrared spectra. A useful diagnostic feature of the infrared spectra of allylic and enol acetates concerns the relative intensities of the C=O and C=C absorptions. In allylic acetates, the former is far more intense, but the intensities are more nearly equal in enol acetates. (b) Identified by comparison of vpc characteristics and infrared spectra with those of an authentic sample. (c) Identified by peak enhancement experiments with an authentic sample. (d) Identified by comparisons of infrared and nmr spectra with those of an authentic sample.

(8) (a) Prepared according to S. Olsen, *Acta Chem. Scand.*, **4**, 901 (1950). (b) Prepared by a modification of the procedure described by P. Z. Bedoukian, *J. Am. Chem. Soc.*, **66**, 1325 (1944). The nmr spectrum indicated a *trans* geometry ($J$ = 12.5 cps). (c) Prepared according to D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952), and shown to be a 60:40 *cis*:*trans* mixture by vpc and nmr studies ($J_{trans}$ = 12.5 cps and $J_{cis}$ = 7 cps).

(9) Contrasting results, the reasons for which are not clear to us, have been very recently reported. Thus, D. R. Bryant, J. E. McKeon, and P. S. Starcher (Abstracts, Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 1965, p 94) describe *trans*-crotyl acetate and 3-buten-1-yl acetate as the major products from oxidation of 1-butene by $Pd(OAc)_2$ in AcOH, with *cis*- or *trans*-2-butene leading to *trans*-crotyl acetate and α-methylallyl acetate in roughly equal amounts. Propene was reported to yield quite high (*ca.* 90%) proportions of allyl acetate. In contrast, a buffered system of $PdCl_2$ in AcOH yields predominantly isopropenyl and propenyl acetates. E. W. Stern, *Proc. Chem. Soc.*, 111 (1963) and I. I. Moiseev, A. D. Belov, and Y. K. Syrkin, *Izv. Akad. Nauk, Ser. Khim.*, No. **8**, 1527 (1963); *Chem. Abstr.*, **59**, 14022 (1963).

**Scheme I**



*secondary* isomer[7b] XIIb. Similarly, *cis*-2-pentene leads very predominantly (>92%) to allylic acetate which is exclusively (>99.5%) *secondary*, 70% isomer[7b] XIIc and 30% XIIIc[7b] being formed.

The above product distributions are from early observations in order to obtain values close to kinetic control proportions. After long reaction times, product isomerizations are evident. For example, allylic isomerization of the allylic acetates occurs, and it was demonstrated separately that primary and secondary allylic acetates, *e.g.*, VIIb and XIIb, are equilibrated by Pd(OAc)$_2$ in AcOH, with concurrent material loss due to other reactions.

As regards allylic ester product, the Pd(OAc)$_2$ oxidation contrasts sharply with its Hg(OAc)$_2$ counterpart.[2] While the latter oxidation gives pure secondary allylic acetate from both 1- and 2-olefins, Pd(OAc)$_2$ gives a separate allylic acetate from each olefin. The nature of the products from the Pd(OAc)$_2$ oxidation and mechanistic considerations cause us to rule out "frozen" or "switching" $\sigma$-allylpalladium species and also $\pi$-allylpalladium counterparts as significant intermediates. An actual study of the rates and products of acetolysis of $\pi$-crotylpalladium acetate confirms that it can be ruled out as an intermediate in the Pd(OAc)$_2$ oxidation of any of the butenes.[10]

The only mechanism for the present Pd(OAc)$_2$ olefin oxidations which appears to accommodate the facts involves oxypalladation,[4] presumably reversible, of the olefin to give the adducts[11] III, IV, VIII, and IX. These eliminate the elements of HPdOAc[12] to yield either enol acetate or allylic acetate depending on the direction of elimination. On this basis, the available data are rationalized in a general way if (i) Markovnikov addition is preferred over non-Markovnikov in oxypalladation, and (ii) elimination to give allylic acetate tends to be preferred over the alternative one leading to enol acetate. This rationalization still leaves the details of stereochemical, conformational, and substituent effects to be clarified before the exact product distributions are more completely understood. Also not clear are solvent or ligand effects on the course of the oxidations. For example, when the Pd(OAc)$_2$ oxidation of 1-butene is performed in a 70 vol. % dimethyl sulfoxide–30% AcOH mixture instead of AcOH, the proportion of allylic acetate, still exclusively primary, in the product rises from the previous 9% to *ca.* 73%.

While oxymercuration–deoxymercuration is incidental to the Hg(OAc)$_2$ allylic oxidation, oxypalladation plays an essential role in the Pd(OAc)$_2$–AcOH allylic oxidation. Reversible oxypalladation–deoxypalladation appears also to provide a mechanism for the allylic isomerization of the allylic esters.[13] Actual comparisons show Pd(OAc)$_2$ in AcOH to be considerably more efficient in this respect than is Hg(OAc)$_2$.

---

[10] W. Kitching and Z. Rappoport, unpublished work.

[11] These are written as monomeric only for simplicity, and not to reflect any information on the actual state of aggregation.

[12] The intimate mechanism here and the mode of formation of the final Pd° are not clear. See E. H. Brooks and F. Glockling, *Chem. Commun.*, 510 (1965), for a recent report of the phosphine-stabilized HPd(PEt$_3$)$_3$Cl.

[13] This type of mechanism seems to apply also to PdX$_2$-catalyzed *trans* esterification of vinylic esters.[8]

**William Kitching, Zvi Rappoport, S. Winstein, W. G. Young**
*Contribution No. 1931, Department of Chemistry*
*University of California, Los Angeles, California 90024*

*Received March 21, 1966*

---

## Adsorption of Nitrogen on Ice at 78°K

*Sir:*

We are currently investigating the physical adsorption of vapors on low-melting adsorbents, *i.e.*, nonionic small molecule substances. Ice is an interesting member of this class and one for which, curiously, no adsorption studies appear to have been published. Possibly related to the present results, however, are those of Karasz, *et al.*,[1] for nitrogen adsorption on TiO$_2$ layered with preadsorbed water.

The ice samples were prepared by condensing water vapor, in the absence of foreign gases, onto a liquid nitrogen cooled glass surface. This was done either *in situ*, using the sample bulb with which the adsorption isotherm was then determined by standard gas volumetric procedure, or in a large flask with the sample

---

[1] F. E. Karasz, W. M. Champion, and G. D. Halsey, Jr., *J. Phys. Chem.*, **60**, 376 (1956).