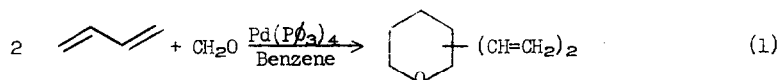


DIVINYLTETRAHYDROPYRANS FROM A NOVEL REACTION OF  
BUTADIENE WITH FORMALDEHYDE

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We have discovered an unexpected novel reaction of butadiene with formaldehyde which occurs under mild conditions (30-80°C) in the presence of catalytic amounts of  $\text{Pd}(\text{P}\phi_3)_4$ . Compounds believed to be isomeric divinyltetrahydropyrans were produced in good yields (>65%) and selectivities (>95%) (eqn. 1), together with traces of higher boilers.

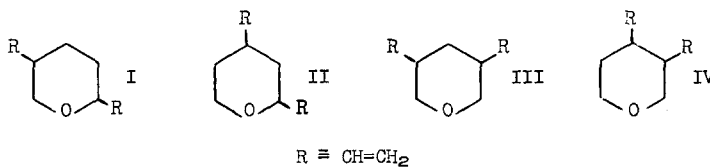


Typically a heterogeneous mixture of butadiene (3 g), benzene (10 ml), formalin solution (3-9 g) and  $\text{Pd}(\text{P}\phi_3)_4$  (0.25 g) was raised to 80°C in an autoclave and kept at autogenic pressures for 22 hours. Distillation of the benzene layer produced a colorless sweet smelling liquid (b.p. 51°C 3 mm) (2.6 g: >65% yield).

This liquid was attributed the formula of  $\text{C}_9\text{H}_{14}\text{O}$  by high resolution mass spectrometry and elemental analysis. Found C, 78.10; H, 10.40; O, 11.50%; calculated for  $\text{C}_9\text{H}_{14}\text{O}$ , C, 78.21; H, 10.21; O, 11.58%. Such a compound is formally derived from one formaldehyde and two butadiene molecules, but these can be combined in a large number of combinations. Further examination showed that the liquid took up two moles of hydrogen gas/mole of product, over  $\text{PtO}_2$  at room temperature, producing another sweet smelling liquid of formula  $\text{C}_9\text{H}_{18}\text{O}$  (mass spectrometry). Evidently two unsaturated bonds and a ring system are present in the original product. I.R. spectroscopy confirmed this showing max at 6.09 (strong) and 5.43 $\mu$  (weak) (attributed

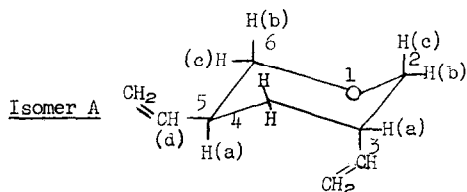
to two  $\text{RCH}=\text{CH}_2$  groups), a band at  $3.25\mu$  ( $\text{CH}_2=$ ),  $7.03\mu$  ( $-\text{CH}_2-$ ) and  $9\mu$  ( $\text{R}-\text{O}-\text{R}$ ). The product was tentatively attributed the divinyltetrahydropyran structure on the basis of these data.

Isomeric structures (I-IV), each with their configurational isomers, are possible products. Careful GLC analysis showed that two products were present in the ratio of 2:1 and almost identical I.R. and mass spectra for the two confirmed them as isomers. Identification was completed using NMR spectroscopy.

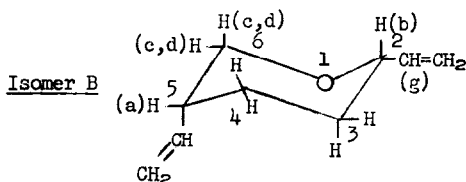


The minor isomer (A) has the simpler NMR spectrum, indicating that it is probably the more symmetrical molecule. Integration demonstrated the presence of six vinylic, two allylic, two methylenic and four O-CH protons; the vinylic proton region is characteristic of terminal vinyl groups. This means that the vinyl groups cannot be on the carbons adjacent to oxygen (positions two or six) and must be on the three, four or five positions.

Irradiation of the allylic protons (1.85 ppm) collapsed some portions of the spectrum. The O-CH proton region simplified from eight lines to four, with production of an AB pattern ( $J = 11.3$  Hz) and the vinylic region was also simplified. The simplicity of the collapsed spectrum in the  $\text{CH}_2-\text{O}$  region suggests that both  $\text{CH}_2-\text{O}$  groups have the same environment, which can be supplied only by the vinyl substituents being in the three and five positions. The proton (1.85 ppm) at position three (or five) shows two gauche couplings ( $J = 2.5$  Hz) to the protons at positions two (or six) (equatorial at 3.25 ppm and axial at 3.45 ppm); consequently, at least one proton at  $\text{C}_3$  or  $\text{C}_5$  must be equatorial. The complexity of the spectrum, together with the small amounts of material available, make more definitive assignment difficult, but the structure below (III) was attributed to isomer A on the basis of the known conformational preferences.



$$\begin{aligned} \nu_a &= 1.85; \nu_b, \nu_c = 3.25 + 3.45; \\ \nu_d &= 5.6 \text{ ppm} \\ J_{ab} &= J_{ac} = 2.5 \text{ Hz} \\ J_{ad} &\approx 6; J_{bc} = -11 \text{ Hz} \end{aligned}$$



$$\begin{aligned}
 V_a &= 2.25; V_b = 3.15; \\
 V_c V_d &= 3.65, 3.90 \text{ ppm} \\
 J_{ac} &= J_{ad} \approx 2.5 \text{ Hz} \\
 J_{bg} &\approx 11; J_{cd} \approx 11 \text{ Hz}
 \end{aligned}$$

The major isomer (B) has a more complex spectrum. Integration showed that there are six vinylic, one allylic, four methylenic and three O-CH protons present. The vinyl pattern is very similar to that observed for A and is characteristic of two terminal vinyl groups, however, the positions of the vinyl groups are different.

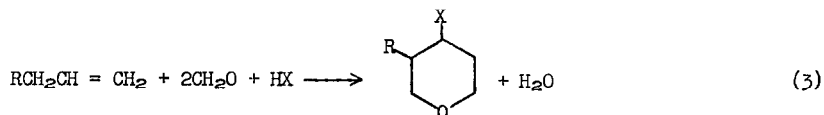
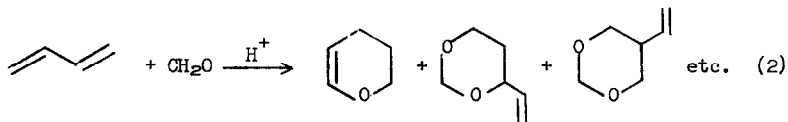
One vinyl group is at the C<sub>2</sub> position, because only three O-CH protons are present and one of these (3.15 ppm) is very different from the other two (3.65 and 3.9 ppm). The proton at C<sub>2</sub> (b) (a triplet,  $J \approx 11$  Hz) shows a coupling of 11 Hz to a vinyl proton (g) and a vicinal coupling of  $\approx 11$  Hz to one vicinal proton at C<sub>3</sub> and  $\approx 0$  Hz coupling to another proton at C<sub>3</sub>. Dihedral angles must be about 180° and 90°. This means that proton (b) at C<sub>2</sub> must be axial, because if the proton were equatorial two gauche couplings of  $\approx 2.3$  Hz would have been observed. This places the vinyl group in the equatorial position.

The other vinyl group is at C<sub>5</sub>. This was established by comparison with the minor isomer where a similar pattern was observed, both before and after decoupling of the allylic proton. The proton at C<sub>5</sub> (a) exhibited two gauche couplings of  $\approx 2.5$  Hz with the two protons at C<sub>6</sub> indicating that proton (a) must be equatorial and the corresponding vinyl substituent axial.

It is necessary to invoke cross-ring coupling between the protons on the four and six positions to explain all the spectrum, but the structure depicted above for B (I) fits well with the observations.

The mechanism of the reaction is not understood although a number of plausible paths can be written involving initial formation of a compound of formaldehyde + bis(triphenylphosphine) palladium followed by insertions of butadiene molecules. Blank experiments ruled out the possible intermediate production of octatrienes<sup>1)</sup> which then react with formaldehyde.

A number of supported palladium catalysts were ineffective as were other potential catalysts based on Pt, Rh, Cu, Ru, Co, Au, Cd, Zn and Ir. The presence of CO did not suppress the reaction but introduced complications because of reaction with the butadiene.



This reaction is distinct from the well-known Prins reaction<sup>2)</sup> (Eqn. 2) which produces a complex mixture of products but no divinyltetrahydropyrans. It is also different from the results recently reported for the acid catalyzed reaction of 1-olefins with formaldehyde at low temperature to give tetrahydropyran derivatives (Eqn. 3). Only complicated mixtures were reported from butadiene-CH<sub>2</sub>O reactions in this work.<sup>3)</sup>

#### References

1. J. F. Kohnle, L. H. Slaugh and K. L. Nakamaye, *J. Amer. Chem. Soc.*, 91, 5904 (1969).
2. V. I. Isagulyants, T. G. Khaimova, V. R. Melikyan and S. V. Pokrovskaya, *Russ. Chem. Rev.*, 37, 17 (1968).
3. P. R. Stapp, *J. Org. Chem.* 34, 479 (1969).

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