THE INTERMEDIACY OF OXETANES IN THE PRINS REACTION

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The electrophilic addition of carbonyl compounds to olefins is generally known as the Prins reaction. Ever since its discovery about fifty years ago, this reaction has been a continuous challenge to synthetic and physical organic chemists[1]. Concerning the mechanism of the Prins reaction, the nature of the intermediate, has been the most debated aspect. The simplest case that can be considered is the acid catalysed reaction of formaldehyde and ethylene:

$$CH_2=CH_2 + CH_2=OH^+ \rightarrow [C_3H_7O]^+ \rightarrow products$$
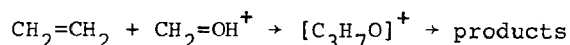
In this study, non-empirical molecular orbital (MO) calculations have been carried out on five isomeric species of $[C_3H_7O]^+$ (I-V) within the self-consistent field (SCF) framework[2] (using the IMBOL-IV system[3] on an IBM 360/65 computer). Standard bond lengths and bond angles were used. In the case of (V) the theoretically optimized[4] geometry of CH_5^+ was incorporated in the input data. The results which are summarized in Fig. 1. indicated that the protonated oxetane (I)
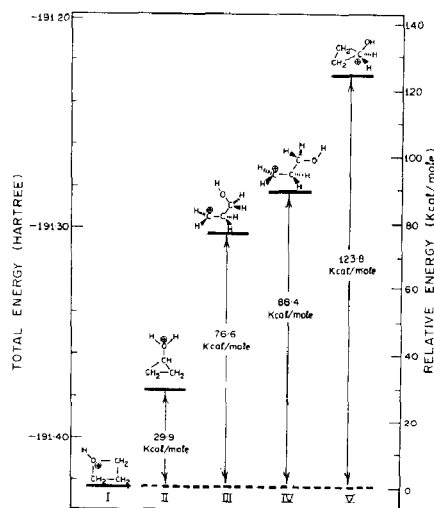

Fig. 1.

can be considered as a very significant intermediate in the Prins reaction. Al-
though the calculated energies relate to protonated species in the gas phase,
the values obtained were useful as qualitative guide as shown below.

To test the predictive potential of these calculations we have deliber-
ately chosen the styrene system where the most often postulated intermediate,
a free carbonium ion would be highly stablized. Reaction of α-methylstyrene
(VI) with two moles of formaldehyde in a heterogeneous system of petroleum
ether and 98% formic acid gave 4-methyl-4-phenyldioxane (VII) in 60.5% yield.
Under similar conditions but using one equivalent of formaldehyde, 2-phenyl-
2-methyloxetane (VIII)[5] gave (VII) in 61% yield (isolated in both cases).

We have then investigated the Prins reaction of Styrene (IX) and the
reaction of 2-phenyloxetane (X)[6] under similar conditions, and also with
solutions of formaldehyde in 88% formic acid. Again, the olefin and the
related oxetane gave identical reaction products, (XI), (XII) and (XIII).
The product distributions, however, varied slightly as shown below:

		(XI)	(XII)	(XIII)
(IX)	(X)	(XI)	(XII)	(XIII)
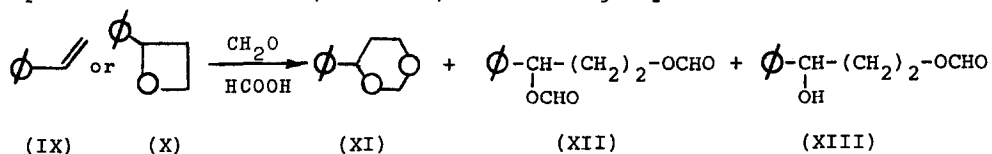
		(XI)	(XII)	(XIII)
from (IX) in 98%HCOOH :		24%	59%	17%
" (IX) in 88% " :		22	46	32
" (X) in 98% " :		15	60	25
" (X) in 88% " :		16	48	36

The dioxane (XI) is a known compound[7], the diformate (XII) gave satis-
factory elemental analysis and could be converted to the corresponding diol
(XIV)[7]. The identity of the monoformate (XIII), supported by elemental ana-
lysis and spectral data, was established by degradation and independent syn-
thesis.

The reactions of (VI) and (VIII), as shown above, demonstrate that the
protonated oxetane (XV) can be a true intermediate in the Prins reaction of
(VI). The Prins reaction of styrene compared with the reaction of (X) under
the same conditions provides further evidence for the intermediacy of oxetanes.
The moderate changes in product distribution offer basis for refinements of a
mechanistic scheme involving protonated oxetanes.

Perhaps the greatest obstacle in the interpretation of Prins reactions with formaldehyde is the complex nature of the acidified solutions of this aldehyde in various solvents. In formic acid, assuming the presence of mono and oligomeric protonated formaldehyde species, our results show that the primary step in the Prins reaction reflects the competition between these to form intermediates of types (XV), (XVI) and (XVII), (XVIII), respectively, where (XVII) and (XVIII) are derived from oligomeric formaldehyde.

(XV), R= CH_3
(XVI), R=H

(XVII), R=CH_3
(XVIII), R=H

$\sim\sim\sim O-CH_2$
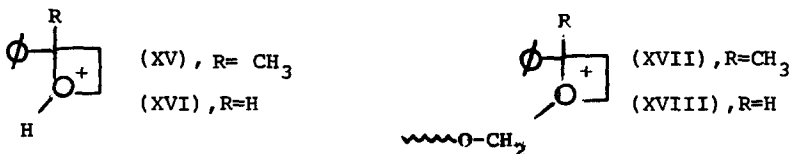
In the case of α-methylstyrene, the intermediate (XV) is protected from external nucleophilic attack at the benzylic position. The only product observed is (VII) which can form from (XVII) by an intramolecular process and from (XV) possibly via (XVII).

In the Prins reaction of styrene, (XVIII) can form dioxane (XI) by a rapid intramolecular reaction while (XVI) is more prone to external nucleophilic attack leading to products other than dioxane. When oxetane (X) is used as a starting material, rapid protonation to (XVI) can be expected which leads to reduced yields of dioxane (XI) and increased proportions of (XII) and (XIII). The isolation of the monoformate (XIII) is interesting and significant. In an excess of formic acid (88 or 98%) the diol (XIV) or (XIII) are rapidly converted into (XII), indicating that free (XIII) is not present in the reaction mixture. Liberation of formaldehyde from reactions conducted with excess of styrene indicates that the hemiacetal (XIX) is originally present and decomposes to (XIII) on work-up.

(XIX)

(XX)

(XXI)
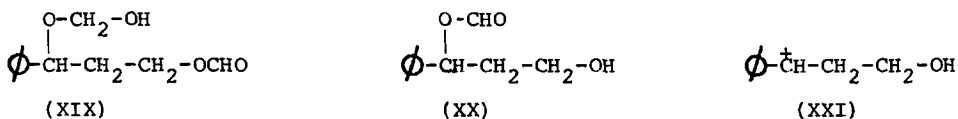
The most likely source of the monoformate precursor (XIX) is (XVI) which offers no possibility for intramolecular dioxane formation. This nucleophilic attack of formaldehyde on (XVI) can, depending on reaction conditions, constitute

another route to dioxane but with a _trans_ stereochemistry. The increased yields of monoformate in 88% formic acid can be rationalized as the result of an increase in the concentration of unprotonated formaldehyde. Thus the recently published results of Wilkins and Marianelli[8] do not exclude the possibility of oxetane intermediates in the Prins reaction. Under our reaction conditions the superb esterifying power of formic acid appears to intercept dioxane formation _via_ external formaldehyde attack on (XVI). Furthermore, we did not find any evidence for the presence of any isomeric monoformate (XX), which, under our reaction conditions would be expected to form from a free carbonium ion (XXI) or the corresponding hemiacetal intermediates.

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