facts discussed above. A similar scheme can also be applied for $^3O_2$ catalysis.

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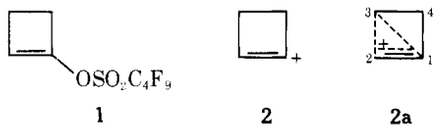
Vinyl Cations. 25.[1] Solvolysis of Cyclobuten-1-yl Nonaflate. Evidence for a Cyclic Vinyl Cation Intermediate

Summary: Cyclobuten-1-yl nonaflate (**1**) solvolyzes in absolute trifluoroethanol via a cyclic vinyl cation intermediate giving rearranged products. Other probable solvolysis mechanisms were experimentally excluded.

Sir: Compared to other ring vinyl derivatives cyclobuten-1-yl nonaflate (**1**) solvolyzes with an exceptionally high reaction rate.[2] This was explained by postulating a cationic intermediate (**2a**) in which the positive charge is stabilized by nonclassical interaction.[3] Earlier MO calculations[4] supported the view that the σ-bond orbitals of C_2–C_3 came into overlap with the vacant p orbital of the cation at C_1 (**2a**). Recent ab initio



calculations are in agreement.[5] (At the completely optimized RHF/STO 3G level, **2a** is 2 kcal/mol less stable than the cyclopropylidene cation, **9**.) To obtain an unambiguous insight into the mechanism of the solvolysis of **1**, we have now carried out several experiments which clearly point out a cyclic vinylic cation intermediate.

Beside the vinyl cation mechanism, other compatible pathways in the solvolysis reactions of cyclobuten-1-yl nonaflate (**1**) are the oxygen–sulfur cleavage and electrophilic/nucleophilic addition–elimination reactions.[2] They have, however, been ruled out by kinetic studies which showed that the solvolysis rate of **1** was independent of the pH in the range of 3.2–9.2.[3] An experiment to exclude the oxygen–sulfur cleavage by conducting the solvolysis of **1** in EtOH–$H_2{}^{18}O$ failed owing to the incorporation of ^{18}O into the cyclobutanone oxygen in a blank experiment. The solvolyses of **1** are always carried out at lower temperatures (~75 °C), while an oxygen–sulfur cleavage, including a nucleophilic attack of the solvent at sulfur as in the case of phenyl triflates, occurs only at higher temperatures.[6]

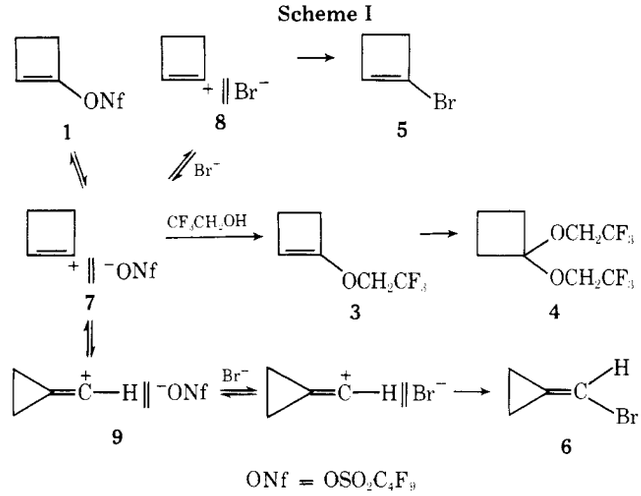
In order to capture the intermediate cyclobuten-1-yl cation, we have now carried out the solvolysis of **1** in absolute trifluoroethanol (TFE) buffered with triethylamine at 75 °C for 10 days. Cyclobuten-1-yl trifluoroethyl ether (**3**) and the ketal (**4**) which were formed[7] in the ratio of 10:1 were isolated by preparative gas chromatography and identified. **3**: NMR δ 4.61 (s, 1 H), 4.18 (q, 2 H), 2.64 (m, 2 H), 2.13 (m, 2 H) ppm; MS *m/e* (rel intensity) 153 (5.5), 152 (61.4, M^+), 151 (6.4), 53 (74.3, cyclobuten-1-ium ion), 39 (base peak, cyclopropenium ion). **4**: NMR δ 3.78 (q, 4 H), 1.6–2.5 (m, 6 H). The formation of the enol ether **3** can be explained only by postulating an intermediate cyclobuten-1-yl cation **2**. The ketal **4** is formed by the addition of TFE to **3**.

An addition–elimination mechanism for the solvolysis of cyclobutenyl nonaflate (**1**) in TFE was excluded unequivocally by carrying out the solvolysis of **1** in absolute CF_3CH_2OD under the conditions mentioned above. The enol ether **3** obtained was examined by GC–MS and found not to contain any deuterium. **3** was separated by preparative gas chromatography and its NMR analysis also showed the complete absence of any deuterium incorporation. The fact that no deuterium was incorporated in **3** rules out an addition–elimination mechanism in the solvolysis of **1**.

A conclusive experiment to prove the intermediate formation of the four-membered cyclic vinyl cation was made as follows. The solvolysis of **1** was carried out in absolute TFE buffered with triethylamine and containing a tenfold excess of tetraethylammonium bromide at 75 °C for 10 days. The product analysis showed that cyclobuten-1-yl bromide (**5**) and cyclopropylidenemethyl bromide (**6**) were formed (53.3% in total) in a ratio of 85:15, along with 34% **3** and 0.9% **4**. The compounds **5** and **6** were identified by GC–MS and NMR spectra, respectively, which were compared with those of authentic samples.[8]

The formation of the bromide **5** and the rearranged cyclopropylidenemethyl bromide (**6**), along with **3** and **4**, are explained as shown in Scheme I, involving ion pairs. In the solvolysis reaction the solvation of the leaving group leads to the solvent separated ion pair **7**. From **7** both the product **3** or the intermediate ion pair **8** are formed which react either with the

Scheme I



ONf = $OSO_2C_4F_9$

solvent or with the nucleophilic bromide leading to **3** and **5**. The rearrangement to form the cyclopropylidenemethyl bromide (**6**) occurs in the solvent separated ion pair **7**. The addition of the excess of tetraethylammonium bromide made the special salt effect possible and the cation **7** had enough time to rearrange and capture the more nucleophilic bromide. This result is in agreement with our earlier work in the solvolysis reactions of other substituted cyclopropylidenemethyl bromides and homopropargyl sulfonates.[9] **5** and **6** are stable under the conditions of solvolysis (75 °C). To bring them to solvolysis, higher temperatures than 75 °C are required.[9]

The next higher homologue of **1**, cyclopenten-1-yl nonaflate and also cyclopenten-1-yl triflate, were recovered practically unchanged even after heating them in an ampule with absolute TFE containing triethylamine as buffer at 100 °C for 10 days. Apparently, cyclopenten-1-yl nonaflate and triflate do not solvolyze with formation of a vinyl cation in TFE, but with an oxygen–sulfur cleavage in the more nucleophilic ethanol/water system.[6]

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(8) Solvolysis of **1** in 80% TFE buffered with TEA containing a tenfold excess of tetraethylammonium bromide gave identical products except for the formation of more cyclobutanone and less of the trifluoroethyl ketal. The other rearranged product, $HC{\equiv}CCH_2CH_2Br$, could not be detected by GC.
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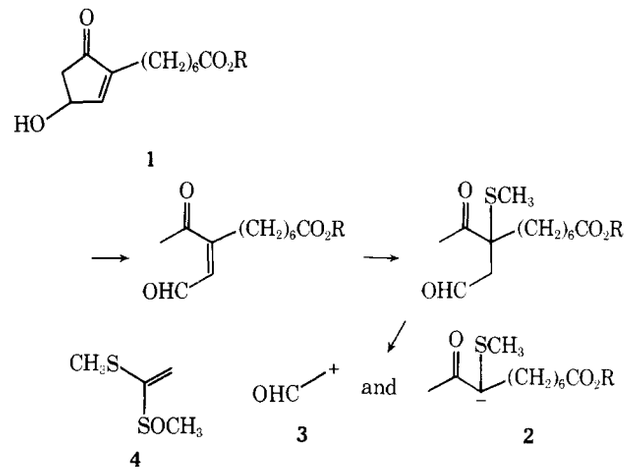
Prostaglandins. An Efficient Synthesis of a 2-Alkyl-4-hydroxycyclopentenone

Summary: The preparation of a 2-alkyl-4-hydroxycyclopentenone precursor to PGE_1 is described. This construction is technically simple to achieve and proceeds in good overall yield.

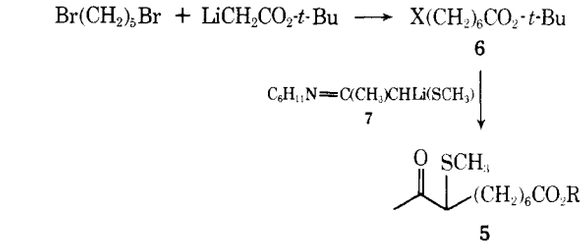
Sir: Hydroxycyclopentenones of type **1** have been shown to be among the most useful of prostaglandin intermediates.[1] We outline here a method for synthesis of **1**, an intermediate leading to PGE_1 and derivatives thereof.

Our construction of **1** arose from the following retro-synthetic consideration which ultimately led to the ketone enolate **2** and the enolonium ion **3**.[2] Efficacy with this scheme has been achieved using the ketene thioacetal monoxide **4**, an experimentally viable equivalent form of enolonium ion **3**.[3]



R = CH_3 or *t*-Bu

The synthesis of **1** (R = CH_3 or *t*-Bu) starts with the ketone ester **5** (R = CH_3 or *t*-Bu) which was conveniently prepared in the following manner. Lithium *tert*-butyl acetate (1 equiv, 1 M in THF, −78 °C)[4] was treated with 1,5-dibromopentane (2 equiv) followed immediately by hexamethylphosphoramide (HMPA, 2 equiv). After the mixture was stirred for 10 min at −78 °C, the temperature of the reaction was raised to 0 °C over 2 h and then quenched with saturated ammonium chloride solution. Standard workup followed by distillation from calcium metal gave the bromo ester **6** (X = Br, bp 80 °C at 0.15 Torr) in 65% yield. This material was converted into the corresponding iodide **6** (X = I, bp 65 °C at 5×10^{-4} Torr) in 97% yield using standard methods.[5] Reaction of **6** (X = I, 0.9 equiv) with the lithium imine salt **7**[6] (1 equiv, 1 M in THF) at −78 °C for 10 h followed by hydrolysis with a mixture of sodium acetate, acetic acid, and water at 25 °C for 45 min gave the ketone ester **5** (R = *t*-Bu) in 86% distilled yield (bp 85 °C at



5×10^{-4} Torr). Treatment of this material with thionyl chloride in THF/CH_3OH solution (1:1) afforded the ketone ester **5** (R = CH_3, bp 65 °C at 5×10^{-4} Torr) in essentially quantitative yield.

The conversion of **5** into the hydroxycyclopentenone **1** was accomplished by the three-step reaction sequence outlined below. Compound **5** (R = CH_3, 1 equiv) was added to a 1 M solution of *tert*-butyl alcohol containing potassium *tert*-butoxide (0.1 equiv). After the mixture was stirred for 10 min at 25 °C, the ketene thioacetal monoxide **4** (1.06 equiv) was added and the resulting mixture stirred for 1 h at 25 °C. Workup with saturated ammonium chloride solution gave the adduct **8** (R = CH_3) in quantitative crude yield.[7] Without purification, **8** (1 equiv) was treated with 48% HBF_4 (0.025 equiv) dissolved in acetonitrile (0.76 M with respect to **8**) at 21–22 °C for 2 h. The reaction mixture was quenched at 0 °C with saturated sodium bicarbonate and the resultant keto aldehyde **9** (R = CH_3) was isolated, again in essentially quantitative yield.[7] The crude keto aldehyde was then cyclized into the hydroxycyclopentenone **1** (R = CH_3) using a phase-transfer technique.[8] Thus, compound **9** (1 equiv) dissolved in benzene (1×10^{-2} M) was treated with a mixture of saturated