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HYDROLYSIS OXIRYLCARBINYL TOSYLATES[1]

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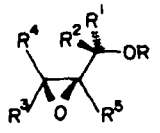
Abstract—The participation of the oxirane carbon–carbon bond during the hydrolysis of oxirylcarbinyl tosylates gives rise to a 2-oxocyclobutyl cation which is further hydrolyzed to β-ketols. The reaction is stereospecific for the *threo* isomers which give only one diastereoisomer, while *erythro* isomers yield a diastereoisomeric mixture of β-ketols. The difference in the hydrolysis rates (*threo* isomers react 1.2–3.6 times faster than *erythro* isomers) can be related to the more important non-bonded interaction in the transition state arising in the *erythro* isomer. A Taft–Streitwieser treatment shows an anchimeric assistance by the oxiryl ring of small amplitude (< 15). This new transposition allows to isomerise an ethylenic ketone by exchanging two substituents.

The cyclopropyl ring has been noted by many authors to behave in a way suggesting an ability to conjugate with a carbonium ion center.[2] In contrast to the rather large amount of data in the literature dealing with the cyclopropyl substitutent, the three membered oxiryl ring has received considerably less attention. This is surprising, as the oxirylcarbinyl system, or products from its solvolysis, are present in a large number of natural products.[3] One interesting aspect of the studies of the participation of the oxiranyl group is in determining if the stabilisation of the electron-deficient carbon is due to the unshared, lone pair of the oxygen, or to a conjugation of the oxiran ring. Some data are in agreement with oxobicyclobutonium cation (from the C–O bond participation) as an intermediate in the rearrangement.[4] In other results an analogy with homoallylic transposition was shown.[5] The oxiryl group is calculated (by semi-empirical INDO calculations) to have a strong stabilizing influence on a cationic site from a slightly distorted bisected alignment.[6]

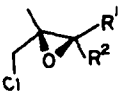
The hydrolysis of oxirylcarbinyl tosylates in the presence of a buffer ($CaCO_3$) was chosen. Acetolysis may lead to an addition reaction on the ring,[4b] and isomerisation in the acidic medium of the tertiary oxirylcarbinols results from proton addition on the oxirane oxygen atom.[7] A heteregeneous medium from pure water and $CaCO_3$ was used in order to increase the solvent polarity and therefore to facilitate the participation reaction.[8]

The epoxide alcohols are prepared by epoxidation of the corresponding allylic alcohols.[9] Epoxidation by *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetate is more stereoselective than epoxidation by a peracid.[10] For example, the epoxidation of *E*-3-methyl-3-penten-2-ol gives **9e** quantitatively, while 2-cyclohexenol is not epoxidized with *tert*-butyl hydroperoxide but is oxidized in cyclohexenone (under the same conditions, cyclohexanol gives cyclohexanone). This result is in contradiction to earlier work.[11]

During tosylate **6** preparation, a chloride **16** is found, resulting from the tosylate being substituted by Cl^- of pyridinium chloride. At 0°C, the reaction is stereospecific and proceeds readily (the reaction must be followed by NMR to avoid the formation of **16**).

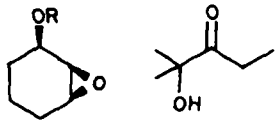


	R = H	R = Ts
$R^1 = R^3 = CH_3$; $R^2 = R^4 = R^5 = H$	**1t**	**2t**
$R^2 = R^3 = CH_3$; $R^1 = R^4 = R^5 = H$	**1e**	**2e**
$R^1 = R^3 = R^4 = CH_3$; $R^2 = R^5 = H$	**3t**	**4t**
$R^1 = R^5 = CH_3$; $R^2 = R^3 = R^4 = H$	**5t**	**6t**
$R^2 = R^5 = CH_3$; $R^1 = R^3 = R^4 = H$	**5e**	**6e**
$R^1 = R^3 = R^5 = CH_3$; $R^2 = R^4 = H$	**7t**	**8t**
$R^2 = R^3 = R^5 = CH_3$; $R^1 = R^4 = H$	**7e**	**8e**
$R^1 = R^4 = R^5 = CH_3$; $R^2 = R^3 = H$	**9t**	**10t**
$R^2 = R^4 = R^5 = CH_3$; $R^1 = R^3 = H$	**9e**	**10e**
$R^1 = CH_3$; $R^3 - R^5 = (CH_2)_4$; $R^2 = R^4 = H$	**11t**	**12t**
$R^2 = CH_3$; $R^3 - R^5 = (CH_2)_4$; $R^1 = R^4 = H$	**11e**	**12e**



6e + TsCl ⟶ **16E**
6t + TsCl ⟶ **16Z**

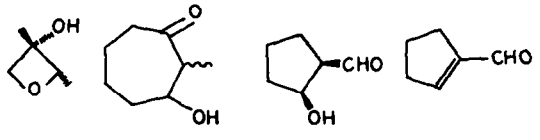
$R^1 = CH_3$; $R^2 = H$ **16E**
$R^1 = H$; $R^2 = CH_3$ **16Z**



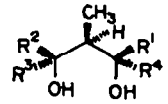
R = H **13**
R = Ts **14**
R = CH_2CF_3 **15**

17

$R^1 = R^2 = H$ **18**
$R^1 = CH_3$; $R^2 = H$ **19e**
$R^2 = CH_3$; $R^1 = H$ **19t**



20 **21** **22** **23**



$R^1 = R^2 = H$; $R^3 = R^4 = CH_3$ meso (2*R*, 3*s*, 4*S*) **24Ms**
$R^1 = R^2 = CH_3$; $R^3 = R^4 = H$ meso (2*R*, 3*r*, 4*S*) **24Mr**
$R^1 = R^3 = CH_3$; $R^2 = R^4 = H$ racemic **24R**

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RESULTS

The hydrolysis of tosylates **2** and **4** occurs without participation:

$$2e \longrightarrow 1e(60\%) + 1t(40\%)$$
$$4t \longrightarrow 17.$$

The ketol **17** is obtained by hydride shift, leading to an oxiryl cation which isomerizes into the α-keto cation precursor of **17** (for α-chloro epoxide opening see ref. 12). The other tosylates give mainly β-ketols:

$$6e \longrightarrow 5t(5\%) + 20(13\%) + 18(82\%)$$
$$6t \longrightarrow 18$$
$$8e \longrightarrow 7t(12.5\%) + 19t(59\%) + 19e(28\%)$$
$$8t \longrightarrow 19e$$
$$10e \longrightarrow 19e(46\%) + 19t(54\%)$$
$$10t \longrightarrow 19t$$
$$12 \longrightarrow 11(30\%) + 21(70\%).$$

The structure of the β-ketols **19e** and **19t** was determined by reduction with $LiAlH_4$ to 3-methylpentane-2,4-diol and comparison of its NMR spectra with those of the four known isomers.[13]†

Ketol **19e** is reduced only in a mixture of diols **24Mr** and racemic **24R**, while ketol **19t** gives diols **24Ms** and **24R**:

$$19e \longrightarrow 24Mr(77\%) + 24R(23\%)$$
$$19t \longrightarrow 24Ms(27.5\%) + 24R(72.5\%).$$

All the β-ketols obtained **18**, **19** and **21** are stable under the reaction conditions (traces of trifluoroacetic acid convert them into the corresponding α–β ethylenic ketones). In contrast, hydrolysis in a buffer medium of tosylate **14** gives mainly cyclopentenecarboxaldehyde **23** which probably comes from the dehydration of intermediate aldol **22**.

$$14 \longrightarrow (22) \longrightarrow 23.$$

When a homogeneous medium is used (water-trifluoroethanol 40/60 w/w), a smaller amount of transposition product is formed as expected and **22** is not isolated. (It is surprising to observe that products **13** and **15** have a *syn* structure: an unexpected retention of configuration during hydrolysis occurs).

$$14 \xrightarrow{H_2O\text{–}TFE} 13(30\%) + 15(20\%) + 23(50\%).$$

†Reduction of β-aminoketones or β-hydroxyketones with chiral centres in both the α and β positions by complex hydrides proceeds without racemisation.[14]

DISCUSSION

β-Ketols are obtained from the hydrolysis of most oxirylcarbinyl tosylates. Therefore we shall discuss as examples, the production of β-ketols from the tosylates **8t** and **8e**. Only one product, the *erythro* β-ketol **19e** is isolated during the hydrolysis of **8t**. Participation of the C–C bond of the oxiran with inversion of configuration on the functional carbon explains the formation of **19e**. The first intermediate is an α-alkoxy cation **25** which is further hydrolysed to a hemiacetal (2-hydroxy oxetane) **26**. This product is not stable in water with a pH near neutrality, on hydrolysis it yields a positive charge on the pro-acyl carbon[15] and retention of configuration of the alkoxy carbon in **19e** (2-alkoxy oxetanes react quantitatively in water[16]).

Hydrolysis of **8e** is not stereospecific, the ketol inversion is only 68% (**7t** is also obtained by a S_N2 mechanism). This different reactivity of **8t** may be due to non-bonded interaction, which is more important in the transition state for the *erythro* isomer **8e**. The observed stereospecificity **8t** requires the C–OTs and C–C bond of oxirane to be antiperiplanar in the conformation leading to the transition state. In the case of **8e**, the interactions between non-bonded atoms are more important for the C–O bond of the oxiran, the C–CH_3 ($R^2 = CH_3$) bond being eclipsed. Thus, ester bond ionisation occurs before the participation process.

Hydrolysis of **10e** affords a mixture of **19e** (46%) (obtained with inversion of configuration) and **19t** because in the conformation leading to the transition state with inversion of configuration an additional interaction due to the *cis* methyl ($R^4 = CH_3$) is involved. The kinetic results for the hydrolysis bear out the proposed mechanism. The first-order solvolysis constants determined as described in the experimental section are summarized in Table 1.

The *threo* isomers (**6t**, **8t**, **10t**) hydrolyse faster than their *erythro* isomers (respectively **6e**, **8e**, **10e**) (Table 2).

For each diastereoisomer, methyl substitution at the β-position (R^3 or $R^4 = CH_3$) causes a rate acceleration. The two effects become larger when the solvent Y value increases.

A Taft–Streitwieser treatment is used to estimate the anchimeric acceleration. The extent of deviations from $\Sigma\sigma^*$ plots are known to provide reliable and quantitative measures of anchimeric assistance.[19] Figure 1 shows that there is kinetic evidence for anchimeric assistance of small magnitude (< 15).

These results are in agreement with the participation of the oxiran C–C bond in the transition state and a localization of a part of the positive charge on β-carbon atom (these results are to be compared with INDO calculations where the bissected conformation a large positive charge is found on this carbon[6]). In the parti-

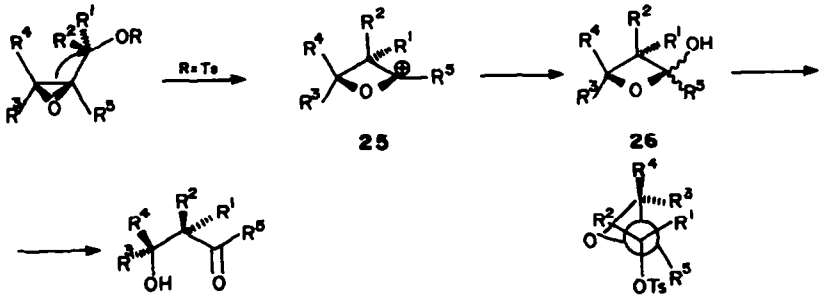


Table 1. Apparent first-order rate constants for the hydrolysis of oxirylcarbinyl tosylates

Compounds	Temp. °C	k × 10⁴ Solvent I[a]	k × 10⁴ Solvent II[a]	k × 10⁴ Solvent III[a]
6t	70[b]	1.8	0.872	—
	80.8	5.1	2.5	—
	91	12.86	6.38	—
6e	70[b]	1.47	0.646	—
	80.8	4.3	2.18	—
	91	11.2	4.48	—
8t	50.2	0.532	—	—
	60.4	1.67	3.36	—
	70	4.62	9.57	—
8e	60.4	0.69	—	—
	70	2.03	2.64	—
	80.8	—	7.91	—
10t	50.2	—	—	1.56
	70	—	7.71	13.9
10e	50.2	—	—	0.58
	60.4	—	—	1.74
	70	—	2.92	4.6
12e	65.5	—	7.34	17.21
	70	—	11.87	27.5
14	60.4	—	—	2.63
	70	—	—	7.24
27[c]	40.1	—	1.72	—
	50.2	—	5.44	—
	60.4	5.26	—	—
	70	12.3	42.6	—

[a]Solvent I: dioxan–water 50/50 v/v (Y-value: 1.361[17]); Solvent II: trifluoroethanol–water 60/40 w/w (Y-value: 1.894[18]); Solvent III: trifluoroethanol–water 40/60 w/w (Y-value: 2.60[18]). Buffer: (−)-nicotin (see experimental part). [b]Values extrapolated. [c]Pinacolyl tosylate.

Table 2. Ratio of the hydrolysis rate constants for the diastereoisomeric tosylates (see Table 1) at 70°

$k_{threo}/k_{erythro}$	Solvent I	Solvent II	Solvent III
k_{6t}/k_{6e}	1.22	1.35	—
k_{8t}/k_{8e}	2.28	3.63	—
k_{10t}/k_{10e}	—	2.64	3.02

Table 3. Acceleration of the hydrolysis rate constants by the β-methyl group (see Table 1) at 70°

β-Methyl/H	Solvent I	Solvent II
threo k_{8t}/k_{6t}	2.57	10.97
erythro k_{8e}/k_{6e}	1.38	4.09
threo k_{10t}—k_{6t}	—	8.84
erythro k_{10e}/k_{6e}	—	4.52

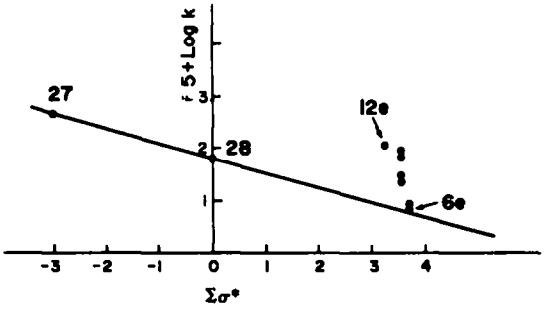
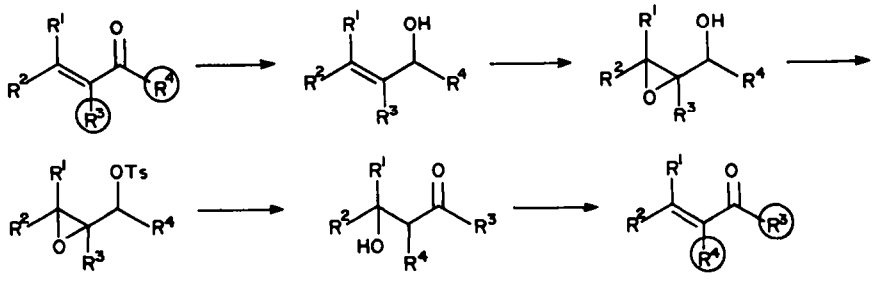


Fig. 1. Rates of solvolysis of secondary tosylates at 70° vs $\Sigma\sigma^*$ (σ^* values taken from ref. 20). Solvent: trifluoroethanol–water 60/40 w/w. $\rho^* = -2.84$. 28: 2-propyl tosylate, calculated rate from data in 50*E*, 70*E* and 97*E*.[21]

cipation reaction, the oxiryl group shows a reactivity analogous to, but greatly weaker than the reactivity of the cyclopropyl ring. It is well known that derivatives of (1-methylcyclopropyl)carbinyl are solvolysed to yield as a major product the 1-methyl-cyclobutyl cation.[22] Similarly, we obtained the 2-methyl-2-oxetanyl cation from oxiranyl derivatives.

CONCLUSION

Hydrolysis of oxirylcarbinyl tosylates yield β-ketols in the most cases. These ketols are obtained with a yield of over 70% to quantitatively. This new transposition analogous to the pinacolic one allows isomerisation of an ethylenic ketone by the following scheme:



For cyclic ethylenic ketones ring expansion occurs when R^2 and R^3 belong to the cycle, and ring contraction occurs when R^2 and R^4 are intracyclic.

This new rearrangement of ethylenic ketones complements 4 others.[23]

EXPERIMENTAL

B.ps are uncorrected. Spectra were recorded on the following instruments: NMR, Varian A-60 spectrometer using TMS as internal standard; IR, Perkin–Elmer 257 spectrometer and mass spec., AEI MS-9 spectrometer. Gas–liquid chromatography was performed on a Varian Aerograph Model 90-P4 using a 10× 3/8 in. 10% Carbowax 20M on 45/60 mesh Chromosorb P.

Preparation of 3-methyl-3-penten-2-ol. The *E*-isomer results from the reduction of the corresponding ketone and the *Z*-isomer is obtained by the literature method.[24] NMR (CCl_4): *E*-isomer: 5.38 (q.), 4.06 (q.); *Z*-isomer: 5.16 (q.), 4.69 (q.).

Preparation of epoxy-alcohols. Allylic alcohols are epoxidized with monoperphtalic acid[9] or $VO(acac)_2$-*t*-BuOOH reagent.[10]

Ratios of diastereoisomeric epoxy-alcohols: **7e/7t**: 98/2; **9e/9t**: 55/45, **11e/11t**: 70/30. NMR (CCl_4): **1** and **3** lit.;[25] **5e**, δ (pattern, J (Hz), J (Hz)): 3.6 (q. 6.2), 2.75 (d. 5.0), 2.47 (d. 5.0), 1.25 (s), 1.13 (d. 6.2); **5t**: 3.47 (q. 6.2), 2.71 (d. 4.8), 2.52 (d. 4.8), 1.27 (s), 1.17 (d. 6.2); **7e**: 3.53 (q. 6.2), 3.02 (q. 5.4), 1.26 (d. 5.4), 1.19 (s), 1.13

(d, 6.2); **7t**: 3.35 (q. 6.4), 2.91 (q. 5.3), 1.26 (d. 5.3) 1.2 (s), 1.12 (d. 6.4); **9e**: 3.56 (q. 6.5), 2.82 (q. 5.7), 1.31 (d. 5.7), 1.20 (s), 1.18 (d. 6.5); **9t**: 3.59 (q. 6.5), 2.84 (q. 5.7), 1.25 (d. 5.7), 1.2 (s), 1.11 (d. 6.5); **11e**: 3.55 (q. 6.2), 3.07 (m), 1.12 (d. 6.2); **11t**: 3.42 (q. 6.2), 3.07 (m.), 1.12 (d. 6.2).

Preparation of oxirylcarbinyl tosylates. Esterification by tosyl chloride was performed according to the standard procedure.[26] The reaction is completed after 8 h for **6** and 24 h for the other tosylates. **6e**: m.p. 52°; **8t**: m.p. 31° (pentane–CCl_4).

Preparation of **16**. Compound **16** was obtained by allowing the appropriate alcohol to react with tosyl chloride during one day at 0°. **16E**: b.p. 55° (35 mm), n_D^{20}: 1.4352 (lit.[27]). NMR AB pattern δ: 3.32 and 3.5 (J = 11.2 Hz), δ (pat. J(Hz)): 2.9 (q. 5.5), 1.35 (s), 1.3 (d. 5.5). **16Z**: b.p. 55° (35 mm), n_D^{20}: 1.4335 (lit.[27]). NMR AB pattern δ: 3.37 and 3.57 (J = 13.5 Hz), δ (pat. J(Hz)): 2.87 (q. 5.5), 1.4 (s), 1.32 (d. 5.5). MS (70 eV) *m/e* (rel. intensity respectively for **16E** and **16Z**): 85 (10, 12), 84 (12, 14), 69 (17, 18), 58 (58, 56), 45 (83, 83), 43 (100, 100), 41 (73, 82), 39 (34, 35).

Hydrolysis of oxiranylcarbinyl tosylates. To a stirred mixture of 400 ml of water and 2 g of $CaCO_3$ and 0.017 mole of tosylate are refluxed during 4 h. After cooling, continuous extraction with ether is carried out for 1 day. The products are separated by preparative gas chromatography.

Hydrolysis of **6e**. Gas chromatography analysis yielded 3 products: **5t**, **20** and **18**. NMR of **20** δ (pat. J(Hz)): 4.68 (q. 6.6), 4.38 and 4.16 (AB, 6.6), 1.31 (s), 1.21 (d. 6.6). NMR of **18**: 3.66 (d. 7.4), 3.63 (d. 5.2), 2.7 (m), 2.15 (s), 1.05 (d. 7.3); MS (70 eV) *m/e* (rel. intensity): 102 (M^+, 2), 87(2), 84(8), 61(40), 59(7), 57(11), 43(100), 42(35), 41(31), 40(5), 39(13), 31(42).

Hydrolysis of **8** *and* **10**. **19e** NMR: δ: 4.02 (q. dedoub. 6.3 and 4), 2.53 (m), 2.17 (s), 1.1 (d. 6.3), 1.07 (d. 6.7). **19t** NMR: δ: 3.83 (q. dedoub. 6.2 and 7.5), 2.52 (m), 2.15 (s), 1.13 (d. 6.2), 1.0 (d. 7.0). Diastereoisomeric proton coupling constants of **19t** and **19e** are found to be 7.5 and 4.0 Hz respectively. Ketols **19** are reduced with $LiAlH_4$ at room temperature and the diols **24** are analysed by gas chromatography in the following order: **24Mr**, **24R** and **24Ms**.

Hydrolysis of **12**. Gas chromatography yielded 3 products **11e**, **11t** and **21**. **21** NMR δ (pat. J(Hz)): 3.9 (m), 2.9 (quint. 7 Hz), 2.4 (m), 1.05 (d. 6.5). To a solution of **21** (100 mg) in CCl_4 was added a drop of trifluoroacetic acid after being heated at 50° during 0.5 h, filtration on alumina, 2-methyl-2-cyclohepten-2-one is obtained. IR (thin film) 1645 cm^{-1}. NMR: δ: 6.8 (t. 6.0), 2.62 (d. 6.0), 1.82 (d. 1.5).

Hydrolysis of **14**. Only one product is obtained **23**.[28] Hydrolysis with water–TFE 40–60: gas chromatography analysis yielded 3 products **23**, **15** and **13**. **15** IR (thin film): 1380, 1260–1210, 860 cm^{-1}. NMR: δ: 3.9 (q. 9.0), 3.17 (s).

Kinetics. Solvent: water–dioxan 50/50 v/v obtained from 47 g of deoxygenated water and 50 g of dioxan.[29] TFE (*purissimum* grade Fluka AG) was dried by distillation from P_2O_5 and then diluted by weight with deoxygenated water to the desired mixture. To 100 ml of a solvent is added 0.486 g (3×10^{-3} mole) of freshly distilled (−)-nicotin and 10 mg of hydroquinon. To 1 ml of solvent is added 2.5×10^{-5} mole of tosylate and this solution is poured into the 1 ml cell of a Perkin–Elmer model 141 electronic polarimeter. The rate of the hydrolysis is observed at 436 mμ by the formation of (+)-nicotin-H^+. Nicotin is a seldom optically active tertiary amine of which the protoned form has an optical activity of opposite signs.[30] Specific rotation varies with the concentration of the liberated acid according to the following relation $[\alpha]_{436}^{25} = 4250(HTsO) - 188.88$; ((−)-nicotin, c: 0.05 M, water, paratoluenesulfonic acid, c: 0.05 M). First order rates were observed in all instances for over 4 half lives. The rates were calculated by a least squares program.[31] By this method, the rate constant of hydrolysis of *tert*-butyl chloride is $k = 5.6 \times 10^{-4}$ at 25°, litt.[18] 7.35×10^{-4} (without buffer) (solvent water–TFE 40/60).

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