THE REACTIONS OF 3-(2-TOSYLOXYETHYL)CYCLOPENTANONE
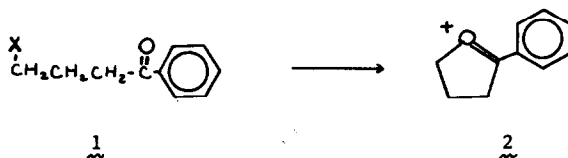
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The carbonyl group of a ketone can enter into nucleophilic reaction with a leaving group in two different ways. First, the oxygen atom can participate, as in the case of 4-halobutyro-phenones (1), to lead to oxonium ions (2).[1] Second, the enol form of the ketone can partici-

pate, as in the case of anti-7-tosyloxybicyclo[2.2.1]heptan-2-one (3), which has been shown to solvolyze via the enol 4.[2] Because of the strained geometry at the C-7 carbon atom the otherwise unreactive tosylate requires assistance for reaction.
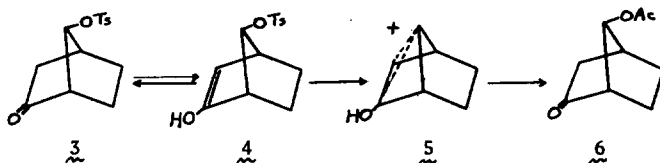

We considered another example of the enol-participation reaction to be possible with 3-(2-tosyloxyethyl)cyclopentanone (7)[3] (see Scheme I). Because of Bredt's rule,[4] the oxonium ion 8 could not exist. However, the primary tosylate, being a less reactive tosylate than a normal secondary one, might desire enough assistance to react via the enols 9 and/or 10, leading to two different ketones, 11 and 12, respectively.

SCHEME I
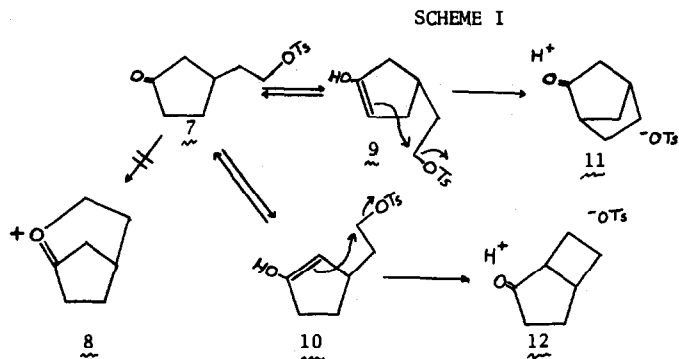
There are two major differences between 7 and 3. First, in the case of 7, **two** enols are possible. Second, with 7 ring closure reactions are possible, analogous to those of 4-(2-tosyloxyethyl)-cyclopentene[5] (13), which acetolyzes to norbornyl acetate (14).

When 7 was solvolyzed in refluxing acetic acid, the normal substitution product, 3-(2-acetoxyethyl)cyclopentanone (15), was the main product, and norcamphor (11) also was observed as a minor product (97:3 respective ratio).
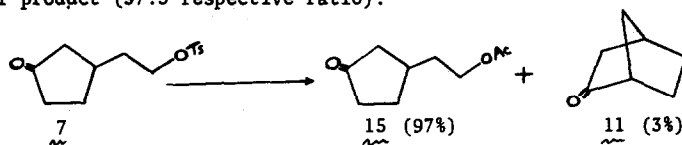
Of the two possible enol-participation products, only norcamphor (11) was observed. Thus, assuming that equilibria of 7 with both 9 and 10 occur (see Scheme II), 9 must react much more rapidly than does 10. This conclusion is consistent with the results obtained with 4-(2-arylsulfonoxy)cyclopentene (16)[5] and 3-(2-arylsulfonoxy)cyclopentene (17)[6,7]: Participation is much more favored in 16 (analogous to the enol 9) than in 17 (analogous to the enol 10).
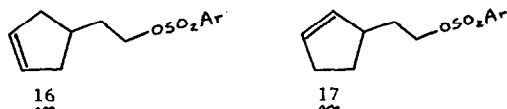
Under varying conditions, 7 gave different ratios of 15:11 (see Table I). With trifluoro-acetic acid, a very poor nucleophile,[8] only norcamphor was observed. In dioxane buffered with

TABLE I

SUBSTITUTION VS. PARTICIPATION IN VARIOUS SOLVENT SYSTEMS

System	%Acetate (15)	%Norcamphor (11)
HOAc-NaOAc	97	3
NaOAc-urea	26	74
HO_2CCF_3-NaO_2CCF_3	0	100
dioxane-urea	0	100

urea,[9] which possesses no nucleophile, precipitating urea-p-toluenesulfonic acid salt[10] indica-

ted the reaction was progressing satisfactorily, and norcamphor was isolated as the sole product.

In acetic acid-urea,[9] the 15:11 ratio was quite different from that in acetic acid buffered

with sodium acetate: the proportion of norcamphor (11) rose to 74%. This increase in the

amount of 11 could be explained by a decrease in the S_n2 component of nucleophilic substitution

owing to the absence of acetate. However, when varying amounts of acetate were used in reac-

tion of 7 with acetic acid, the 15:11 ratio remained essentially the same (see Table II). Thus

the S_n2 contribution must be negligible. Since the S_n1 contribution would be expected to be

constant, the only explanation for the changes in urea-acetic acid would be that more enol 9

exists, and that the equilibrium involving 9 must be shifted in favor of 9.

TABLE II

SUBSTITUTION VS. PARTICIPATION IN HOAc-NaOAc

Molarity, 7	Molarity, NaOAc	%Norcamphor (11)
0.071	0.100	3.6
0.0191	0.050	2.2
0.0364	0.050	3.0
0.0174	0.025	3.5
0.0087	0.0125	2.6

In an attempt to force the reaction to give both bicyclic ketones, the keto tosylate 7

was reacted with sodium hydride in tetrahydrofuran. It was thought that both enolates 18 and

19 would be formed irreversibly, and thus would have to go on to the respective bicyclic

ketones 11 and 12 (see Scheme 11). However, reaction of 7 with sodium hydride in refluxing

tetrahydrofuran for 24 hours led only to norcamphor (11). Assuming that both enolates were

formed, the results mean that a pathway exists between 18 and 19; apparently an equilibrium

was set up between the two enols. The drive for 18 to participate was so much greater than

that for 19 that the total reaction product came about via the former enol. Thus, the results

for enolate participation were those of enol participation.

SCHEME II
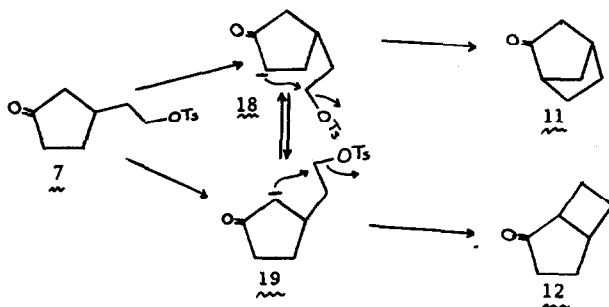
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