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DIHYDROQUINOLONES VI (1)

Unusual fragmentation of a heterocyclic ring upon sulfur-ylide treatment

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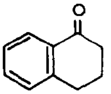
The unexpected results of some base-catalyzed condensation reactions of dihydroquinolones (2) led to a further study of its reactions in strongly alkaline medium.

The effective nucleophile, dimethylsulphoxonium methylide, was initially reacted with the tetralone 1, upon which the expected epoxyde 2 was isolated.



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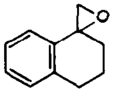

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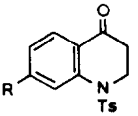
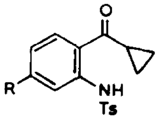


3 R = H

4 R = OCH_3



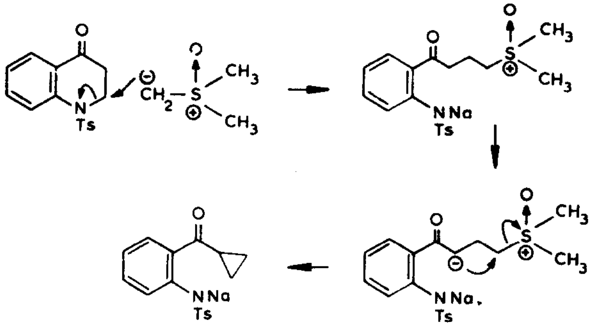
5 R = H

6 R = OCH_3

Ts = $-SO_2-C_6H_4-CH_3$

On the contrary, however, when the reaction was carried out with the quinolone 3 no product was isolated upon ether-tetrahydrofuran extraction of the DMSO-water layer. When the water layer was acidified, a product crystallized which after purification showed a m.p. of 104-106°C. Its structure 5 was assigned on the basis of the following data : IR, 1635 cm^{-1} (C=O), NMR δ ($CDCl_3$) 1.0 m (cyclopropyl CH_2-CH_2), 2.33 s ($ArCH_3$), 2.5 m (-CH cyclopropyl), 7.0-8.1 (aromatic) and 11.30 s (-NH) ppm; in the mass spectrum a molecular-ion peak was present at m/e 315, while significant fragment losses of 41 (cyclopropyl) and 69 (CO-cyclopropyl) mass units provide additional support for the structure of 5. In the same manner a crystalline material, with m.p. 134-135°C, was obtained from the reaction of quinolone 4 and the ylide, and shown to be 6. The unexpected cleavage of the heterocyclic ring under influence of strong nucleophiles is rationalized in schema I. Of significant interest thereby is the first step of the reaction in which the unprecedented substitution of the ylid carbanion on a saturated carbon is of theoretical interest.

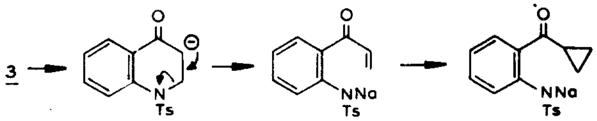
Scheme I



Although the alkylation of phosphorus ylides is a known process (3), contrary to the alkylation of sulphoxonium ylides, no examples have been reported in which a N-tosyl anion is displaced in such a reaction. The other steps in scheme I need no further comment.

An alternative explanation for the observed reaction course (4), which is based on a prior E_2-type of elimination of the N-Ts moiety and subsequent insertion of the sulphoxonium methylid in the C=C bond (scheme II), was rejected on the following grounds. Firstly, none of the expected olefinic ketone is obtained on treatment of the quinolone 3 with base, and secondly, when the reactions of 3 and 4 were carried out with dimethylsulphonium methylid the identical cyclopropane ketones 5 and 6 were obtained.

Scheme II



In view of the kwnon preference of the latter ylide to form epoxides (5), rather than cyclopropane insertion products in the reaction with α,β-unsaturated ketones, the lack of formation of any epoxide provides strong support for a reaction course as described in scheme I.

Further investigations on the reaction of S-ylides and other nucleophilic reagents with appropriately substituted dihydroquinolones are in progress.

References

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