

SYNTHESIS AND PYROLYSIS OF CARBONATE TOSYLHYDRAZONE
SALTS DERIVED FROM VICINAL GLYCOLS

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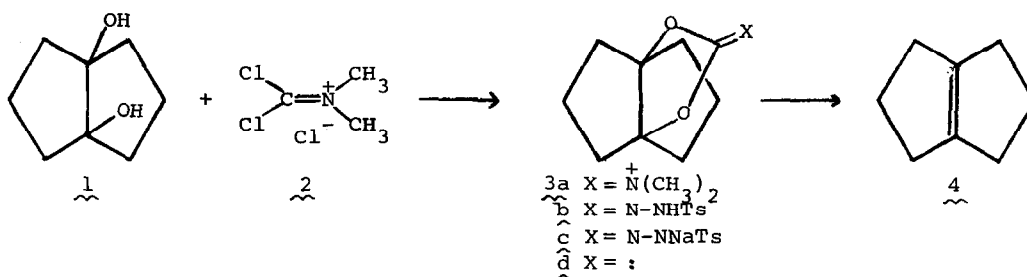
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As a model for the synthesis of a class of theoretically interesting olefins from the corresponding diols,¹ we undertook a study of the conversion of bicyclo[3. 3. 0]octane-1, 5-diol (1) to $\Delta^{1,5}$ bicyclo[3. 3. 0]-octene (4).¹ Although a number of synthetic methods² accomplished this transformation with varying degrees of success and convenience, none proved readily adaptable to olefin synthesis under conditions where the product, as it was formed, could be immediately trapped at low temperature for spectroscopic study.³ We therefore investigated vacuum pyrolysis of the carbonate tosylhydrazone (CTH) salt (3c) derived from 1. Pyrolysis of such a CTH salt would be expected to yield the 2-carbena-1, 3-dioxolane (3d), since alkoxy⁴ and dialkoxy⁵ carbenes have been prepared by this method. Based on the fragmentation of the parent 2-carbena-1, 3-dioxolane,⁶ as well as its dithio analog,⁷ to ethylene, we anticipated that this reaction might provide a new method for the conversion of diols into olefins,⁸ which would permit rapid low temperature product isolation.

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Since most routes to related hydrazones^{4a, 5, 7} involve formation of imines or immonium salts as synthetic intermediates, in devising a general method for the conversion of vicinal diols into their CTH derivatives, we noted with interest the report that "phosgene immonium chloride" (2) reacts with catechol to give a cyclic immonium salt.⁹ We found that refluxing equimolar amounts of 1 and 2 in CH_2Cl_2 (dried over molecular sieves) for an hour under argon gave the hygroscopic immonium salt (3a). The solvent was removed; and in a typical preparation starting with 25 mmol of 1, an equivalent amount of tosylhydrazine, 8 ml of triethylamine (dried over KOH), and 70 ml of dry tetrahydrofuran were added to the freshly prepared salt in a glove bag. The mixture was heated at reflux under argon for two hours, cooled in an ice bath, and suction filtered to remove precipitated triethylammonium chloride. The filtrate, containing 3b, was added dropwise to 1.1 equivalents of sodium hydride and then heated at reflux for 1.5 hours. The sodium salt (3c) that precipitated was filtered, washed with pentane, and dried in a vacuum dessicator. The salt (ir: 1690 cm^{-1} , KBr), prepared as described above, was obtained in 95% yield, based on starting diol, and appeared pure by nmr. A satisfactory analysis was obtained from a sample of the hydrazone (3b) (mp $175\text{-}176^\circ$, dec.), prepared from 3c by dissolving the salt in water, extracting with CHCl_3 , and recrystallizing the crude hydrazone once from CH_2Cl_2 --petroleum ether.

The sodium salt (3c) was pyrolyzed under vacuum at 0.02 torr by placing it in a flask attached to a cold trap and submerging the flask in an oil bath heated above 300° . Decomposition of the salt began around 290° , and was accompanied by formation of sodium *p*-toluenesulfinate and evolution of CO_2 (and presumably N_2). The olefin (4) was obtained from the cold trap in 80% isolated yield and in greater than 98% purity. The decomposition could also be run in refluxing tetraglyme and a concentrated pentane solution of the olefin isolated by extraction followed by distillation. Not only was the latter method less convenient; but it also gave only a 50% yield of 4, as determined by glc analysis of the concentrated pentane solution.

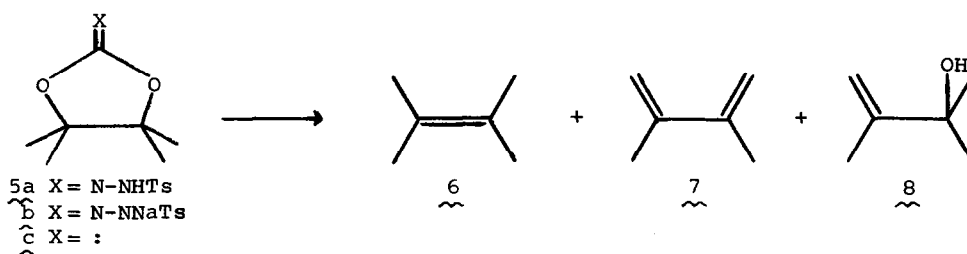


In order to test the generality of CTH salt pyrolysis as a method of olefin synthesis, pinacol was converted by the procedure described above to its CTH derivative (5a; mp 140-141°, dec; satisfactory analysis) and thence to the CTH salt (5b; ir: 1700 cm⁻¹, KBr). Pyrolysis at 290° under vacuum did give tetramethylethylene (6), but 2,3-dimethylbutadiene (7) and 2,3-dimethylbuten-3-ol (8) were also found in the cold trap. The ratio of 6 : 7 : 8 was 10 : 3 : 1, and the overall yield of products was 70%. The same three products were formed when 5b was pyrolyzed in tetraglyme.¹⁰

The formation of the latter two products is easily explained by mechanisms involving homolytic cleavage of one bond between an oxygen and a tetravalent carbon in the presumed 2-carbena-1,3-dioxolane intermediate (5c).¹¹ Although 6 could be generated by concerted loss of CO₂ from 5c,^{4b} part or all of it might be formed from the same biradical intermediate from which 7 and 8 arise. If 7 and 8 are formed from only that fraction of the biradical that has undergone rotation about the central C-C bond, thus making formation of the planar olefin by CO₂ loss impossible, the absence of similar products from the pyrolysis of 3c is understandable; since the diradical resulting from one-bond cleavage in 3d cannot undergo such internal rotation.

The formation of 7 and 8 in the pyrolysis of 5b also has interesting implications with regard to the mechanism of the Corey-Winter reaction.^{2a} When the thionocarbonate derived from pinacol is heated in triethyl phosphite at 150°, the only product is 6; no 7 or 8 is detected.¹² If 5c is indeed produced by the pyrolysis of 5b, then our results suggest¹³ that such a free 2-carbena-1,3-dioxolane may not be an intermediate in the Corey-Winter reaction.¹⁴

Further mechanistic studies and synthetic applications of CTH salt pyrolysis are in progress.



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- ¹⁰The products were separated by distillation from the cooled tetraglyme at reduced pressure. No significance is necessarily attached to the fact that the relative proportions of the products isolated varied somewhat between the dry and solution pyrolyses, since 6, 7, and 8 differ in their relative volatilities. In fact, in small scale dry pyrolyses, where overall yields were lower than 70%, the product mixture was found to contain a larger proportion of 8, presumably due to some loss of the more volatile 6 and 7. In addition to 6, 7, and 8 several other products were detected, but they were formed in amounts too small to permit characterization.
- ¹¹Analogy for this process is found in the reactions of alkoxy⁴ and dialkoxy⁵ carbenes.
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- ¹³Experiments designed to allow arylsulfonylhydrazone salt decomposition under conditions more nearly identical to those of the Corey-Winter reaction are in progress. We have found that replacement of toluene by p-nitrobenzene as the aryl group allows salt decomposition at considerably lower temperatures.
- ¹⁴Phosphite ylides have been proposed as intermediates in the formation of olefins from trithiocarbonates.
- ¹⁵Similar intermediates might be generated from thioncarbonates and undergo decomposition directly to olefins without the intermediacy of free 2-carbena-1,3-dioxolanes.
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