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OXYGEN YLIDES - II .
PHOTOCHEMICAL AND RHODIUM-CATALYZED REACTIONS OF DIAZOMETHANE WITH (S)-2-METHYLOXETANE

Wolfgang Kirmse* and Pham Van Chiem

Abteilung für Chemie der Ruhr-Universität Bochum
Postfach 102148, D-4630 Bochum, Federal Republic of Germany

Volker Schurig

Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Federal Republic of Germany

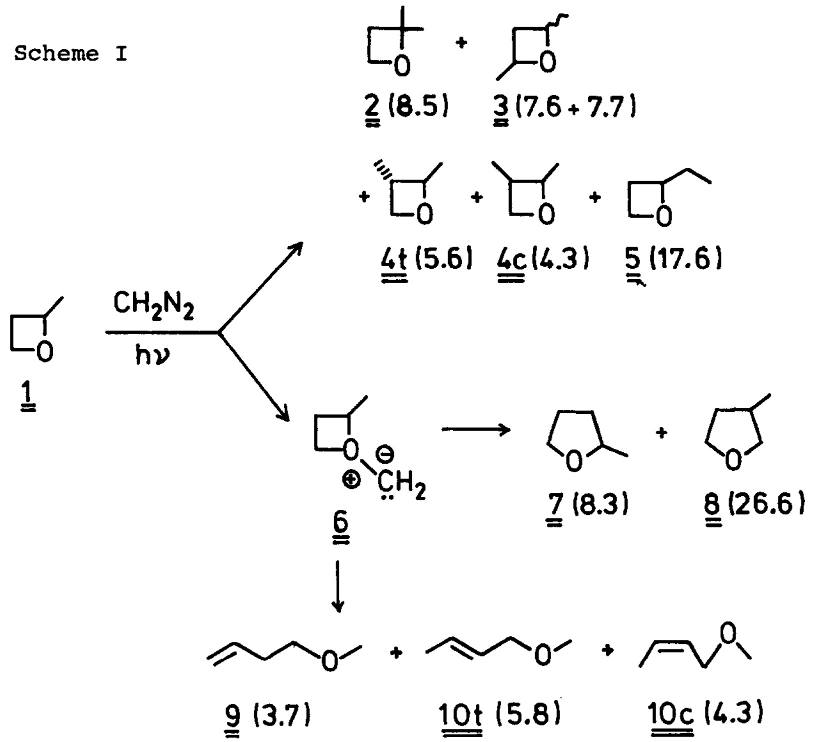
SUMMARY Photolysis of diazomethane in (S)-2-methyloxetane gives 2- and 3-methyltetrahydrofuran (1:3.2), the latter being formed with 21 % net retention of configuration. In contrast, rhodium acetate catalysis yields racemic 3-methyltetrahydrofuran exclusively.

[1,2]-Carbon shifts (Stevens rearrangements) of ammonium[1] and sulfonium ylides[2] have been extensively investigated with respect to mechanism, stereochemistry, and application in synthesis. To our knowledge, no comparable study of oxonium ylides is available. The efficient ring expansion reaction of oxetane with carbenes has recently been shown to proceed via capturable oxonium ylides.[3] Appropriately substituted oxetanes provide the opportunity to scrutinize the regioselectivity and stereoselectivity of the Stevens rearrangement. Here we communicate our results with 2-methyloxetane.

Dilute solutions of diazomethane in 2-methyloxetane (1)[4] were photolyzed by means of a medium-pressure mercury arc (pyrex vessel, 0°C). The resulting mixture containing 11 products and starting material was analyzed by GC on capillary columns (120-150 m, coated with polypropylene glycol, 50-70°C). All products (Scheme I) were identified by comparison with authentic samples. 2,2-Dimethyloxetane (2),[5] 2,3-dimethyloxetane (4),[6] 2-ethyloxetane (5),[7] and the methoxybutenes (9,10)[8] were prepared according to literature procedures; 2- and 3-methylfuran (7,8) are commercially available. 2,4-Dimethyloxetane (3) was obtained from 4-chloro-2-pentanol by the general method of Searles[4] as a mixture of isomers (39:61). We have not been able to separate the stereoisomers on a preparative scale and to assign their configurations unambiguously. In contrast, the isomers of 2,3-dimethyloxetane (4) separate readily, and analysis of their spectra is conclusive.[9]

C-H insertion accounts for 51 % of the products. The relative reactivities of 2-H (tertiary), 3-H (secondary), 4-H (secondary), and CH_3 (primary), corrected for the number of hydrogens, are 1.7:1:1.55:1.2. Very similar results have been obtained for oxetane.[3] The present data indicate some deac-

Scheme I

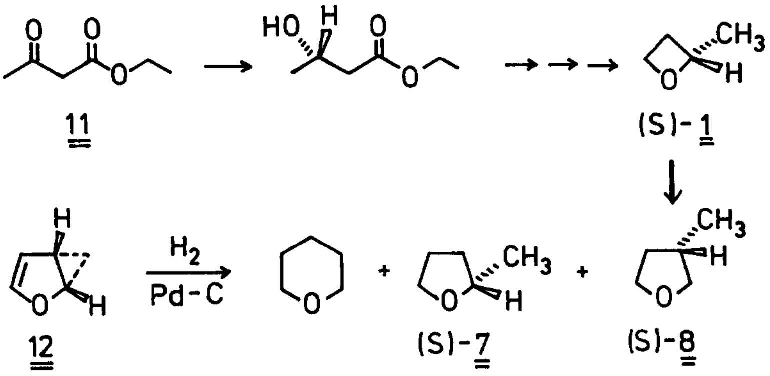


tivation of 3-H which is less reactive than the methyl C-H bonds. This effect enhances the α:β ratio. Insertion into the 3-H bonds shows slight steric discrimination in favor of trans isomer 4t which is not observed with the 4-H bonds.

Ylide 6 undergoes 1,2-carbon shifts in competition with intramolecular β-elimination. Proton transfer to the ylidic carbon favors 3-H over CH_3 by a factor of 4. Models indicate a more favorable (less strained) transition state for elimination of the methyl hydrogens, provided that 2-CH_3 and the ylidic carbon are cis to each other. The low yield of 9 then suggests that the trans configuration of ylide 6 predominates. The 1,2-carbon shift leads to 2- and 3-methyltetrahydrofuran (7 and 8, respectively) in a 1:3.2 ratio. Preferential migration of the tertiary carbon is in accordance with the radical-pair mechanism of the Stevens rearrangement.[10-13]

For a stereochemical analysis of the 1,2-carbon shift we required optically active 2-methyloxetane as solvent. We therefore preferred a short route to optical impure (S)-1, starting with fermenting yeast reduction of ethyl acetoacetate (11),[14,15] to the more elaborate synthesis of optically pure (S)-1 from (2S,3S)-allothreonine.[16] Photolysis of diazomethane in (S)-1 (e.e. 67 %) yielded 3-methyltetrahydrofuran (8) of 14 % e.e. The enantiomeric purities were determined by complexation gas chromatography on optically active metal complexes.[17,18] GC of the multi-component photolysis mixture on chiral columns proved to be impractical. Fortunately, we were able to isolate 8 (but not 7) by preparative GC. Thus the e.e. of 8 was readily analyzed but its configuration remained to be assigned. Hydrogenation of optically active

Scheme II



2-oxabicyclo[3.1.0]hex-3-ene (12), partially resolved by chromatography on triacetylcellulose,[19] provided 7 and 8 of identical configuration. Correlation of 8 with authentic (S)-2-methyltetrahydrofuran[20] was thus achieved, and the (S)-configuration of 8 from the ring expansion of (S)-1 was established (Scheme II). Partial retention at the migrating carbon is general for 1,2-shifts proceeding by a sequence of dissoziation and recombination.[10-13]

When gaseous diazomethane was introduced into solutions of rhodium(II)acetate (30 mg) in (S)-1 (6 ml) and pentane (20 ml), racemic 3-methyltetrahydrofuran (8) (e.e. < 2 %) was formed with high selectivity (> 95 %), albeit in low yield (ca. 5 %, based on diazomethane). Although rhodium carbenoids undergo C-H insertion with hydrocarbons[21],this process is completely suppressed in favor of attack at the oxetane oxygen. Moreover, ring expansion predominates to the virtual exclusion of β-elimination; the regioselectivity and the stereochemistry of the Stevens rearrangement are also affected. These observations indicate that rhodium remains attached to the ylidic carbon of 6 throughout its subsequent reactions. The selectivity displayed by rhodium carbenoids in competitive cyclopropanations of olefins has been attributed to the development of positive charge in the transition state.[22] Similar ideas - accommodation of the negative charge by rhodium and development of positive charge on the migrating carbon - would also explain the enhanced regioselectivity and complete racemization encountered in the catalyzed Stevens rearrangement.

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