

Oxetanes from Photocycloaddition of 2-Aminopropenenitriles to Methyl Phenylglyoxylate and Benzils

Christiane van Wolven^a, Dietrich Döpp^a, and Gerald Henkel^b

^a Fachbereich Chemie, Universität Duisburg-Essen, D-47048 Duisburg, Germany

^b Department Chemie und Chemietechnik, Fakultät Naturwissenschaften, Universität Paderborn, D-33098 Paderborn, Germany

Reprint requests to Prof. Dr. D. Döpp. Fax: +49(0)203-379-4192. E-mail: doepp@uni-duisburg.de

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By irradiation of methyl phenylglyoxylate (**1**) in benzene solution in presence of equimolar amounts of 2-aminopropenenitriles $\text{H}_2\text{C}=\text{C}(\text{NR}_2)\text{CN}$ (**3a–e**, NR_2 = morpholino, 1-pyrrolidinyl, 1-piperidinyl, hexamethyleneimino, heptamethyleneimino) the corresponding $2R^*,3R^*$ head-to-head oxetanes **4a–e** were obtained in moderate yields (11 – 52%) along with 2 – 28% of *rac*-dimethyl 2,3-diphenyltartrate (**2**). In presence of (*S*)-2-(2-methoxymethylpiperidin-1-yl)propenenitrile ((+)-**3g**) **1** is transformed into 26% of **2** and 33% of a mixture of diastereomeric oxetanes **4g,4'g** in a ratio of 1.4 : 1 which could be improved to 2.5 : 1 by preparative layer chromatography. The absolute configuration of the major diastereomer **4g** was unambiguously confirmed by a single crystal X-ray structure determination to be $2R,3R,2'S$. Analogous photoadditions to benzil (**5a**), 4,4'-bis-(trifluoromethyl)benzil (**5b**) and 4,4'-dichlorobenzil (**5c**) with (+)-**3g** and its lower homologue (*S*)-2-(2-methoxymethylpyrrolidin-1-yl)propenenitrile ((-)-**3f**) gave oxetanes only in low yield as detected by ^1H NMR. By-products arise from competitive symmetrical α -cleavage of **5**.

Key words: Paternò-Büchi Reaction, Ketene Equivalents, Asymmetric Induction, Diastereoselectivity, X-Ray Structure Analysis