[2+2]CYCLOADDITION REACTION OF CYCLOHEXENONE, MALEIC ANHYDRIDE, AND MALEIMIDE DERIVATIVES TO EXO-METHYLENE DOUBLE BOND OF DIKETENE

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The photoreaction of diketene with isophorone gave 8-hydroxy-4,4,6-trimethyl-2-oxobicyclo[4.2.0]octan-8-ylacetic acid β-lactone (1) and 7-hydroxy-4,4,6-trimethyl-2-oxobicyclo[4.2.0]octan-7-ylacetic acid β-lactone (2). Compound (1) was treated with aniline to give 3-anilino-1-hydroxy-5,7,7-trimethylbicyclo[3.3.1]nonan-2-ene-2-carboxanilide (3), which was hydrolyzed to 1,3-dihydroxy derivative (4).

The photoreaction of diketene with 3-acetoxy-5,5-dimethyl-2-cyclohexenone gave *rel*-(1*R*,6*S*,7*S*)-6-acetoxy-7-hydroxy-4,4-dimethyl-2-oxobicyclo[4.2.0]octan-7-ylacetic acid β-lactone (5a) and its *rel*-(1*R*,6*S*,7*R*) isomer (5b). Compound (5a) was treated with dimethylamine to afford 2,6-dioxocyclooctanylacetamide derivative (6). On the other hand, compound (5b) was treated with dimethylamine to give *rel*-(1*R*,6*S*,7*R*)-6-acetoxy-7-hydroxy-4,4-dimethyl-2-oxobicyclo[4.2.0]octan-7-ylacetic acid (7).

Diketene reacted with dimedone under irradiation to give 1-hydroxy-4,4-dimethyl-2,6-dioxocyclooctan-1-ylacetic acid β-lactone (8) and 4,4-dimethyl-2,6-dioxobicyclo-[5.1.0]octan-1-ylacetic acid (9). Compound (8) was hydrolyzed to compound (9).

Photoreaction of diketene with maleic anhydride and N-phenylmaleimide gave 2-oxo-1-oxaspiro[3.3]heptane-5,6-dicarboxylic anhydride (10) and 2-oxo-N-phenyl-1-oxaspiro[3.3]heptane-5,6-dicarboximide (11), respectively. Alcoholysis of compound (10) and (11) gave the same product, dimethyl 5-methoxycarbonyl-3-oxoheptanedioate (12).