

91. Photochemical Synthesis of 2-Alkylidene-1,3-cycloalkanediones

Preliminary Communication

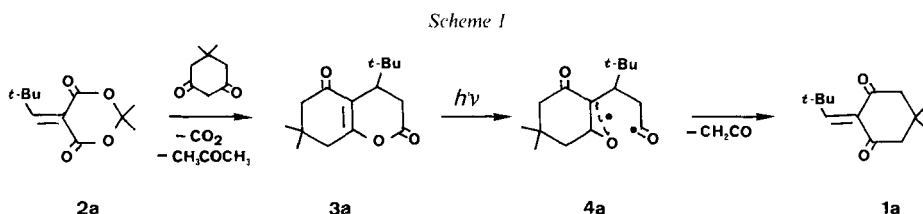
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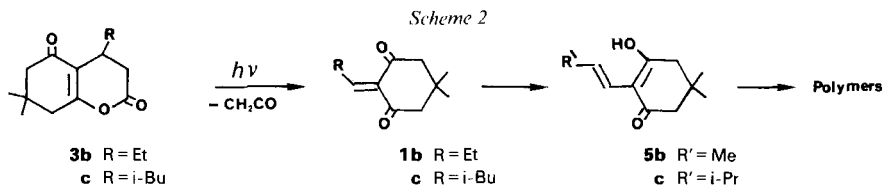
(3.III.87)

Photolysis ($\lambda = 254$ nm) of 4-(*tert*-butyl)-4,6,7,8-tetrahydro-7,7-dimethyl-2*H*-1-benzopyran-2,5(3*H*)-dione (**3a**) in *t*-BuOH affords 2-(2,2-dimethylpropylidene)-5,5-dimethyl-1,3-cyclohexanedione (**1a**) in 80% yield *via* homolysis of the lactone O–CO bond and subsequent ketene elimination.

Dimedone (5,5-dimethyl-1,3-cyclohexanedione) is a well known reagent for the characterisation of aldehydes [1] [2]. Products are formed from one molecule of the aldehyde and two molecules of dimedone, the reaction sequence consisting of a *Knoevenagel* condensation followed by a *Michael* addition, this second step proceeding much faster than the first one, due to the fact that the primarily formed alkylidene- or (arylalkylidene)dimedones **1** are extremely strong *Michael* acceptors [3], and, therefore, are neither detected nor isolated in such reactions. Some time ago, we had communicated the synthesis of two such formal 1:1 condensation products of an aromatic aldehyde and dimedone *via* MeOH elimination from the corresponding benzyl methyl ethers [4]. We now report the first synthesis of an alkylidenedimedone, 2-(2,2-dimethylpropylidene)-5,5-dimethyl-1,3-cyclohexanedione (**1a**), achieved by a light-induced reaction (*Scheme 1*).



In contrast to cyclic 1,3-diketones, *Meldrum's* acid (2,2-dimethyl-1,3-dioxane-4,6-dione) affords 1:1 condensation products **2** with aldehydes [3]. Compounds **2** are known [5] to react with dimedone in a *Michael* addition to give 4,6,7,8-tetrahydro-2*H*-1-benzopyran-2,5(3*H*)-diones **3**. In such a reaction, **2a** [6] gives **3a** in 77% yield. Irradiation ($\lambda = 254$ nm) of **3a** in *t*-BuOH affords **1a** in 80% yield, most probably by ketene elimination from the acyl-vinyloxy biradical **4a** [7] [8] (*Scheme 1*). Up to now, ketene extrusion in the photolysis of 6-membered enol lactones has only been observed once as a side reaction [9].



Irradiation of benzopyrandiones **3b** and **3c** under similar conditions gave polymeric material only. It can be assumed that alkyldenedimedones **1b** and **1c** tautomerise to alkenyldimedones **5**, which, being 1,3-dienes, undergo consecutive photochemical reactions (Scheme 2).

On the one side, the sequence **2a** → **1a** represents just one example of a promising general method for the synthesis of 2-alkylidene derivatives of cyclic 1,3-diketones, as dimedone can be substituted by other cyclic diketones, e.g. 1,3-cyclopentanedione. On the other side, restrictions regarding the substituent on C(4) of the pyran ring have to be taken into consideration.

Experimental Part

General. See [10]. Irradiations were performed in a Rayonet RPR-100 photoreactor on Ar-degassed solns. using 254-nm lamps.

4-(*tert*-Butyl)-4,6,7,8-tetrahydro-7,7-dimethyl-2H-1-benzopyran-2,5(3H)-dione (**3a**). From **2a** and dimedone according to [5] in 77% yield, m.p. 105°. IR (CCl₄): 1790, 1670, 1645. MS: 250 (5, M⁺), 166.

4-Ethyl-4,6,7,8-tetrahydro-7,7-dimethyl- and 4,6,7,8-Tetrahydro-4-isobutyl-7,7-dimethyl-2H-1-benzopyran-2,5(3H)-diones (**3b** and **3c**, resp.). These were prepared from dimedone and the corresponding acrylic acids according to [11] in 51 and 55% yield, resp. **3b**: m.p. 33°. **3c**: m.p. 52°.

Photolysis of 3a. A soln. of 500 mg (2 · 10⁻³ mol) of **3a** in 10 ml of *t*-BuOH was irradiated for 50 h, the reaction being monitored by GC on a SE 30 capillary column. Evaporation of the solvent and bulb-to-bulb distillation (140–145°/15 Torr) afforded 345 mg (80%) of 2-(2,2-dimethylpropylidene)-5,5-dimethyl-1,3-cyclohexanedione (**1a**) as colourless liquid, GC purity > 98%. ¹H-NMR (C₆D₆): 7.40 (s, 1H); 2.11, 2.09 (2 s, 2H); 1.20 (s, 9H); 0.59 (s, 6H). MS: 208 (37, M⁺), 193.

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