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

Preliminary Communication

by **Klaus Hobel** and **Paul Margaretha***

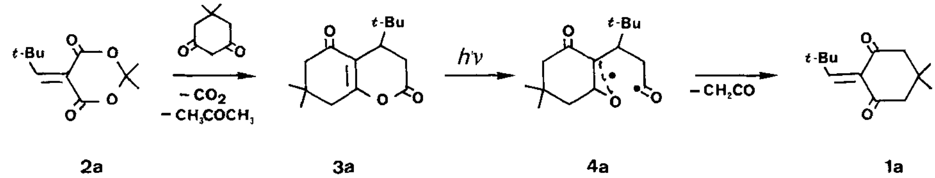
Institut für Organische Chemie, Universität, D-2000 Hamburg 13

(3.III.87)

Photolysis (λ = 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.

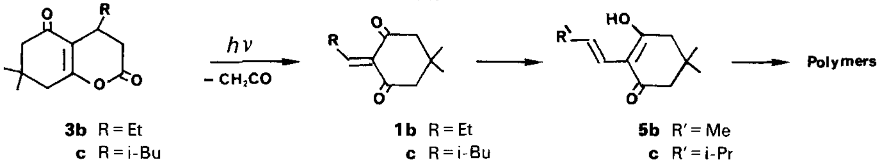
Dimedone (5,5-dimethyl-1,3-cyclohexanedione) is a well known reagent for the characterisation of aldehydes [1] [2]. Products are formed from one molecule of the aldehyde and two molecules of dimedone, the reaction sequence consisting of a *Knoevenagel* condensation followed by a *Michael* addition, this 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)*.

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 (λ = 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].

Scheme 2



Irradiation of benzopyrandiones **3b** and **3c** under similar conditions gave polymeric material only. It can be assumed that alkylidenedimedones **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-2*H*-1-benzopyran-2,5(3*H*)-dione* (**3a**). From **2a** and dimedone according to [5] in 77% yield, m.p. 105°. IR (CCl_4): 1790, 1670, 1645. MS: 250 (5, $M^{+\cdot}$), *166*.

*4-Ethyl-4,6,7,8-tetrahydro-7,7-dimethyl- and 4,6,7,8-Tetrahydro-4-isobutyl-7,7-dimethyl-2*H*-1-benzopyran-2,5(3*H*)-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 ($2 \cdot 10^{-3}$ 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 (C_6D_6): 7.40 (*s*, 1H); 2.11, 2.09 (2 *s*, 2H); 1.20 (*s*, 9H); 0.59 (*s*, 6H). MS: 208 (37, $M^{+\cdot}$), *193*.

REFERENCES

[1] E.C. Horning, M.G. Horning, *J. Org. Chem.* **1946,** *11,* 95.
[2] L.F. Fieser, M. Fieser, in 'Reagents for Organic Synthesis', Wiley & Sons, New York, 1967, Vol. 1, p. 266.
[3] F.J. Kunz, P. Margaretha, O.E. Polansky, *Chimia* **1970,** 165.
[4] P. Margaretha, O.E. Polansky, *Monatsh. Chem.* **1970,** *101,* 824.
[5] P. Margaretha, *Tetrahedron Lett.* **1970,** 1449.
[6] P. Schuster, O.E. Polansky, F. Wessely, *Monatsh. Chem.* **1964,** *95,* 53.
[7] D. Bellus, *Adv. Photochem.* **1971,** *8,* 109.
[8] H. Hombrecher, P. Margaretha, *J. Chem. Soc., Chem. Commun.* **1986,** 1477.
[9] A. Yogev, Y. Mazur, *J. Am. Chem. Soc.* **1965,** *87,* 3520.
[10] H. Hombrecher, P. Margaretha, P. Tissot, *Helv. Chim. Acta* **1986,** *69,* 1681.
[11] B. Monroe, *J. Heterocycl. Chem.* **1969,** *6,* 917.