Tetrahedron Letters Vol. 21, pp 4589 - 4592
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0040-4039/80/1122-4589$02.00/0

A NOVEL SOLVOLYTIC REARRANGEMENT OF 2,2-DIMETHYL-5-(1-BROMOMETHYLETHYLIDENE)-1 ,3-DIOXANE-4,6-DIONE

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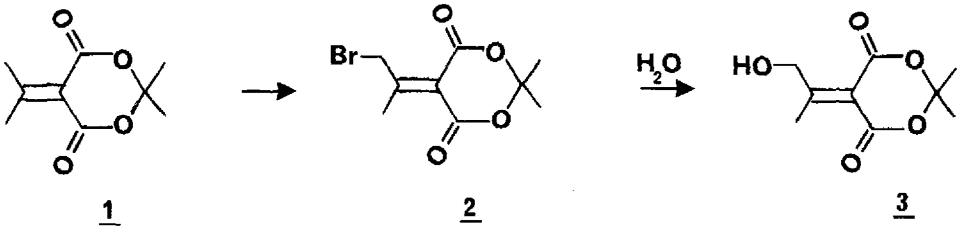
Treatment of the title compound under basic aqueous conditions leads to 2,2-dimethyl-5-(2-ketopropyl)-1,3-dioxane-4,6-dione; the structure and mechanism of formation of this compound is described.

In the course of other work involving the synthesis of $\Delta^{\alpha,\beta}$-butenolides[1] we required the hydroxy compound 3 which we proposed to synthesize from 2,2-dimethyl-5-(1-methylethylidene) -1,3-dioxane4,6-dione (1) (obtained from Meldrum's acid[2] and acetone according to the procedure of Lehnert[3]) by the process outlined in Scheme 1.

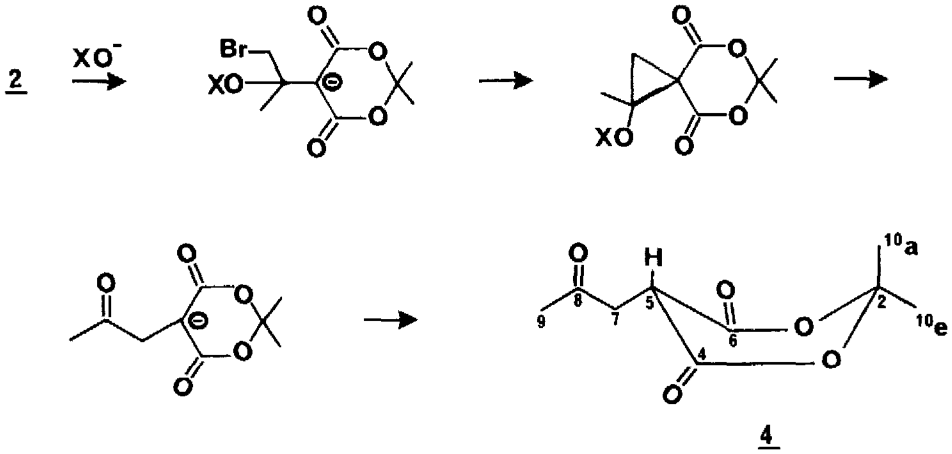


Scheme 1.

Treatment of an ice-bath cooled solution of 1 in CCl_4 with 1.2 equivalents of N-bromosuccinimide under irradiation from a 250 watt light bulb over a period of 10 hours gave, after standard workup and recrystallization of the product, an 81% yield of a mixture of the bromide 2 and the corresponding symmetrical dibromide (approx. 25%). Flash chromatography[4] and repeated recrystallization from CCl_4-pentane gave pure 2[5,6].

Treatment of a sample of 2 (containing approximately 20% of the dibromide as determined by nmr analysis) with K_2CO_3 in aqueous tetrahydrofuran gave, on workup and recrystallization (benzene-chloroform) a single compound (mp 151-3°) in 67% overall yield based on 1. The elemental analysis[5] and mass spectrum[6] established the formula of this product as $C_6H_{12}O_5$. The 90 MHz ^1H-nmr spectrum[7] ($CDCl_3$) indicated the presence of two isochronous methyl groups at 1.82 ppm, a single methyl group at 2.24 ppm and mutally coupled (J = 4.4 Hz) signals for two hydrogens (d) at 3.28 ppm and one hydrogen (t) at 3.85 ppm. Exchange of acidic protons with D_2O lead to the collapse of the doublet at 3.28 ppm to a singlet and the disappearance of the peak at 3.85 ppm. The infrared spectrum (Nujol), however, was not consistent with the hydroxy compound 3 as it indicated the presence of a carbonyl absorption at 1718 cm^{-1} in addition to the normal carbonyl absorptions[9] of Meldrum's acid derivatives at 1750 and 1785 cm^{-1}.

Consideration of the spectral information suggested that compound 2 had undergone a rearrangement to 2,2-dimethyl-5-(2-ketopropyl)-1,3-dioxane-4,6-dione (4). Given the known stability of the Meldrum's acid carbanion[10] and the propensity of alkylidene Meldrum's acid derivatives to undergo nucleophilic addition[11] a reasonable mechanism for the solvolytic rearrangement of 2 to 4 is given below (Scheme 2)[12].



Scheme 2.

Obviously in the D_2O exchange experiment the acidic proton at C-5 is exchanged causing the disappearance of the peak at 3.85 ppm and thecollapse of the doublet at 3.28 ppm (due to the C-7 hydrogens) to a singlet.

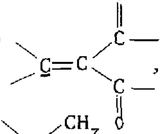
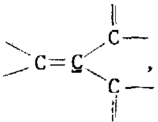
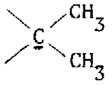
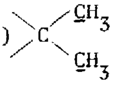
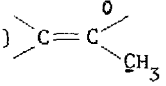
Confirmation of the assignment of the structure of the rearrangement product as 2,2-dimethyl-5-(2-ketopropyl)-1,3-dioxane-4,6-dione (**4**) was obtained from the ^{13}C-nmr spectrum[7,8]. The assignments of the ^{13}C chemical shifts as well as the C-H coupling constants are summarized below[13].

^{13}C-nmr Assignments for **4**

Carbon	δ (ppm) (multiplicity)		^1J(Hz)	^2J and ^3J(Hz)	
8	203.9	(m)	-	$J_{C_8-H_{7,9}}$	6.0
4,6	165.3	(d of t)	-	J_{CO-H_5} 9.0, J_{CO-H_7}	4.6
2	105.4	(m)	-	$J_{C_2-H_{10a,e}}$	4.6
5	41.9	(d of t)	125.2	$J_{C_5-H_7}$	4.2
7	40.2	(t of q)	131.1	$J_{C_7-H_9}$	1.7
9	29.2	(q)	127.9	-	-
10e	28.3	(q of q)	129.2	$J_{C_{10e}-H_{10a}}$	3.2
10a	26.9	(q of q)	128.8	$J_{C_{10a}-H_{10e}}$	3.1

References and Notes

1. For a leading reference to butenolide synthesis see: A. S. Berg and P. Kolsaker, Acta Chem. Scand., B32, 665 (1978).
2. Meldrum's acid 2,2-dimethyl-1,3-dioxane-4,6-dione.
3. W. Lehnert, Tetrahedron 29, 635 (1973). See also E. Campaigne and J. C. Beckman, Synthesis 1978, 385.
4. W. C. Still, M. Kahn and A. Mitra, J. Org. Chem., 43, 2923 (1978).

5. Satisfactory elemental analysis was obtained for this compound. (Guelph Chemical Laboratories Ltd.).
6. <u>Cmpd 2</u>: Mass Spectrum: M^+ 261, 263, m/e 247, 249 (M^+-methyl), base peak m/e 125; Infrared: ν_{max}^{Nujol} 1765, 1732 (carbonyls), 1630 cm^{-1} ($>C=C<$).
^{1}H-nmr: $\delta_{CDCl_3}^{TMS}$ (ppm) 1.77 (6H,s), 2.60 (3H, s), 4.67 (2H, s).
^{13}C-nmr: $\delta_{CDCl_3}^{TMS}$ (ppm): 168.9 (s)

$>\underline{C}=C(C(=O)-)_2$, 160.6 (s) and 160.3 (s) $>\underline{C}=O$'s,
117.8 (s)

$>C=\underline{C}(C(=O)-)_2$, 104.3 (s)

$>\underline{C}(CH_3)_2$, 31.4 (t) Br-$\underline{C}H_2$- , 27.2 (q)

$>C(\underline{C}H_3)_2$
and 23.3 (q)

$>C=C(-)\underline{C}H_3$

<u>cmpd 4</u>: Mass spectrum: M^+ 200, m/e 185 (M^+-methyl), m/e 158 (M^+-$C(CH_3)_2$), m/e 142 (M^+ - $OC(CH_3)_2$).
7. The ^{13}C-nmr and 90 MHz ^{1}H-nmr spectra were recorded by Kirk Marat on a Bruker WH-90 Spectrometer. Compound **2** was run in the off resonance decoupled mode and compound **3** was run in both the undecoupled and broad-band decoupled modes.
8. For a discussion of the ^{13}C-nmr spectra and conformation of 1,3-dioxane-4,6-dione derivatives see: P. Äyräs, Acta Chem. Scand., B <u>30</u>, 957 (1976).
9. R. A. Abramovitch, Can. J. Chem., <u>37</u>, 361 (1959).
10. For a review of the physical and chemical properties of Meldrum's acid see: H. McNab, Chem. Soc. Rev., <u>1978</u>, 345.
11. C. F. Bernascmi and G. D. Leonarduzzi, J. Amer. Chem. Soc., <u>102</u>, 1361 (1980).
12. Under the conditions of the reaction the nucleophile could conceivable be any one of HO^-, HCO_3^-, $CO_3^=$ or H_2O.
13. This research was supported by operating grants from the Natural Sciences and Engineering Research Council of Canada (formerly the National Research Council) and the Research Board of the University of Manitoba.

(Received in USA 2 July 1980)