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A NEW ROUTE TO CYCLOPENTANE-1,3-DIONES

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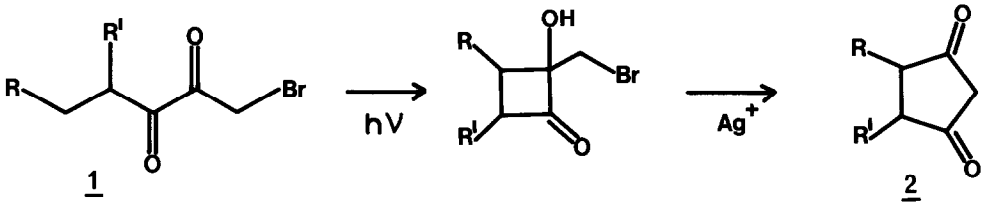
Summary: 2-Bromomethyl-2-hydroxycyclobutanones undergo ring expansion to substituted cyclopentane-1,3-diones in the presence of silver ion.

Cyclopentane-1,3-diones are valuable synthetic intermediates and over recent years several routes to these compounds have been devised.[1] However many of these are not adapted to the preparation of cyclopentanediones unsubstituted at the 2 position or require the relatively expensive cyclopentane-1,3-dione as starting material. We report here that the Ag^+ induced solvolysis of 2-bromomethyl-2-hydroxcyclobutanones from photocyclisation of α-bromomethyl-1,2-diketones[2] provides a simple route to many 4 and 4,5 substituted cyclopentane-1,3-diones.



1 2

No cyclopentane-1,3-dione was obtained from 1b due to failure of the photocyclisation reaction. This failure is a consequence of very inefficient intramolecular H abstraction from an unactivated methyl by the triplet diketone moiety[3] permitting competing processes (presumably C-Br cleavage) to take precedence. Thus the products from 1e are those resulting from H abstraction from the methylene rather than the methyl group. The lower yield of product from 1d also reflects less efficient photocyclisation (as evidenced by lower quantum yield and presence of other carbonyl compounds in addition to cyclobutanones in the photolysate) which is, probably due to steric constraints affecting the initial H abstraction of the subsequent diradical cyclisation. In all cases the sterochemistry of the final product is determined by the configuration at C-3 in the intermediate cyclobutanone.

When 2-bromomethyl-2-hydroxy-indan-1-one[3] was treated with Ag^+ under similar conditions separation of the silver bromide was much slower accompanied by extensive blackening of the mixture. No dihydroxynaphthalenes were isolable and in view of the low oxidation potential of such compounds[8] it seems probable that they are oxidised by the Ag^+.

Typical procedure: A solution of the diketone (5mmol, 95% purity) in methyl acetate (50 ml) containing 2,6 lutidine (0.25 mmol) was irradiated at 0° under N_2 until the starting

material was consumed. The solvent was removed in vacuo at room temperature, the residue taken up in acetic acid (4 ml), then a solution of silver nitrate (1g) in aqueous acetic acid (4 ml 1:1 v/v) added. After standing at 0° under N_2 until separation of silver bromide ceased (4-6hr) there was added a solution of the lithium bromide (0.25g) and sodium acetate (0.35g) in the minimum amount of water and the precipitate filtered off. Evaporation of the filtrate in vacuo < 40°C followed by flash chromatography of the residue on silica using ethyl acetate/hexane/acetic acid (50:50:2.5) as eluent gave the product. The cis and trans isomers of 2e were separated by tlc on silica using the same solvent system.

Table

Diketone		Cyclopentane dione (Yield)	Reference
1a	R = Me_2, R' = H	2a (72%)	4
1b	R = H, R' = H	---	
1c	R = Ph, R' = H	2c (64%)	5
1d	R,R' = $-(CH_2)_4-$	2d (35%, cis)	6
1e	R = Me, R' = Me	2e (36% trans; 25% cis)	7

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5. 2a: m.p. 125-126°C. ^{1}H-NMR ($CDCl_3$) 2.55 (dd, J=18, 2.6 Hz, 1H) 3.00 (dd, J=18, 7 Hz, 1H), 3.8 (dd, J=7, 2.6 Hz, 1H), 5.3 (s, 1H), 6.5 (bs, OH), 7.74 (m, 5H).

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7. 2e trans; oil, ^{1}H-NMR ($CDCl_3$) 1.21 (d, J=7.1 Hz, 6H) 2.40 (m, 2H) 5.2 (s, 1H) 8.1 (bs, OH); 2e cis; oil, 1.11 (d, J=7.1 Hz, 6H) 2.78 (m, 2H) 5.2 (s, 1H) (7.8 (bs, OH). Both cis and trans had M^+ 127 with fragmentation pattern as reported[9] for 15/85 mixture of the two isomers.

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