Tetrahedron Letters No. 39, pp 3505 - 3508, 1977. Pergamon Press. Printed in Great Britain.

REGIOSPECIFIC SYNTHESIS OF α-METHYLENE-KETALS AND-KETONES

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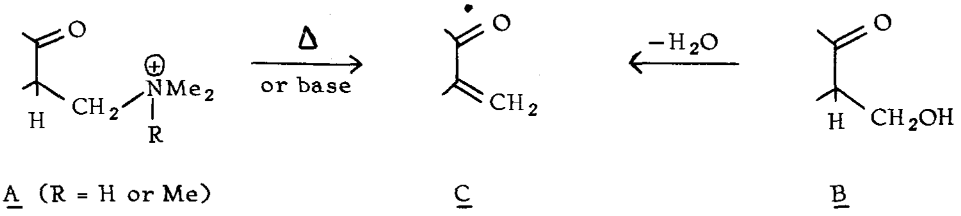
(Received in UK 25 July 1977; accepted for publication 8 August 1977)

Synthetic routes to α-methylene carbonyl compounds C have received considerable attention (1 - 4). Most of them involve either a β-elimination from Mannich salts A (1 - 3) or dehydratation of α-hydroxymethyl-ketones B (2, 4). Direct obtention of C from corresponding saturated ketones is sometimes possible (5).



The main difficulties encountered in these reactions are the low regiospecific yield when starting with unsymmetrical ketones (6) and the relatively low stability of enones of the type C (2). Several steps sequencies leading to one product only (1,2,7,8) (in order to avoid mixtures which are difficult to separate) are time consuming.

The purpose of the present communication is to point out a simple preparation of α-methylene-ketones C starting from α-keto-ketals D (9). The first step is a Wittig reaction (10) (D ⟶ E) followed by mild deketalization with wet silicagel (11).

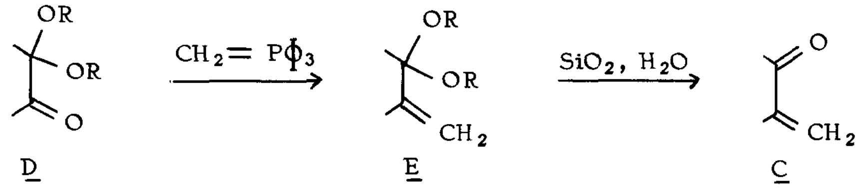


Table I shows the remarkable yields of our reaction. Best results were obtained by using t-AmONa as a base (10). The products are easily isolated from contaminating t-AmOH and $POΦ_3$ by bulb to bulb distillation or column chromatography.

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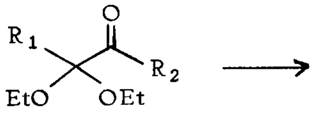
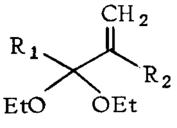
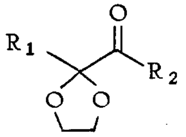
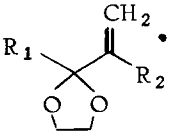
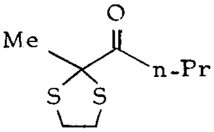
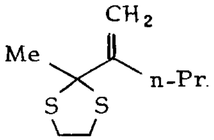
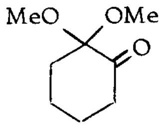
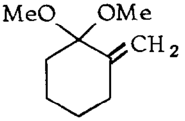
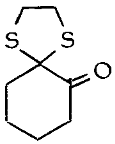
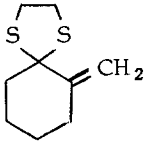
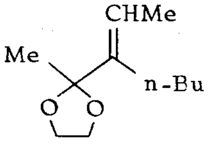
Table I. - Obtention of α-methylene-ketals and -thioketals.

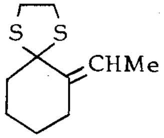
α-keto-ketals or -thioketals (9)	α-methylene-ketals or -thioketals		Yields[a] (%)
 1	 6	R_1 = Me ; R_2 = n-Bu (a) R_1 = Me ; R_2 = i-Pr (b) R_1 = Et ; R_2 = n-Bu (c)	75 78 84
 2	 7	R_1 = Me ; R_2 = n-Pr (a) R_1 = Me ; R_2 = n-Bu (b) R_1 = Me ; R_2 = sec-Bu (c) R_1 = n-Pr ; R_2 = Me (d)	95 90 72 80
 3	 8		95
 4	 9		80
 5	 10		80

a) 6a-c and 9 are isolated by distillation, 7a-d, 8 and 10 by column chromatography.

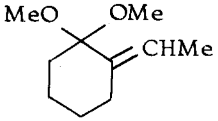
Other ketals or thioketals of α-ethylenic carbonyl compounds 11 - 14, may be obtained the same way ($EtP\phi_3Br$ or $i\text{-}PrP\phi_3Br$ and t-AmONa)



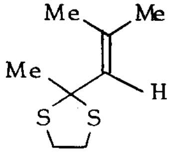
11 74%



12 71%



13 80%

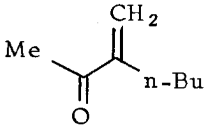


14 70%

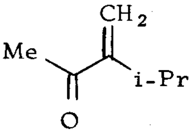
(all of them are isolated by distillation).

Alternatively, preparation of ketals of α-ethylenic carbonyl compounds is sometimes possible from corresponding carbonyl compounds (12) or, most often, from saturated ketones (13) but their yields are generally lower.

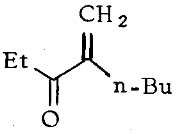
Deketalizations (e.g. 6 a - c, 7b, 9, 13) with wet silicagel (11) give very good results. For instance α-ethylenic-ketones 15 - 19 are obtained almost quantitatively without decomposition or migration of the double bond (14) (for comparison with other procedures for obtaining some of these α-ethylenic-ketones see ref. 2, 15, 16).



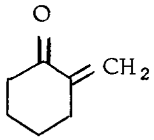
15 95%
(from 6a and 7b)



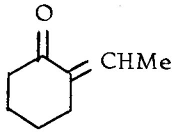
16 95%



17 92%



18 91%



19 90%

Significant dethioketalizations (of 8, 10, 12, 14) was however not achieved.

It appears clearly that the regiospecific sequency D ⟶ E ⟶ C gives good overall yields for methylene- as well as for other alkylidene-ketones.

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