

A MILD CLEAVAGE OF 1,3-DIKETONES: PREPARATION OF
2-ACYL-1,3-DITHIANES

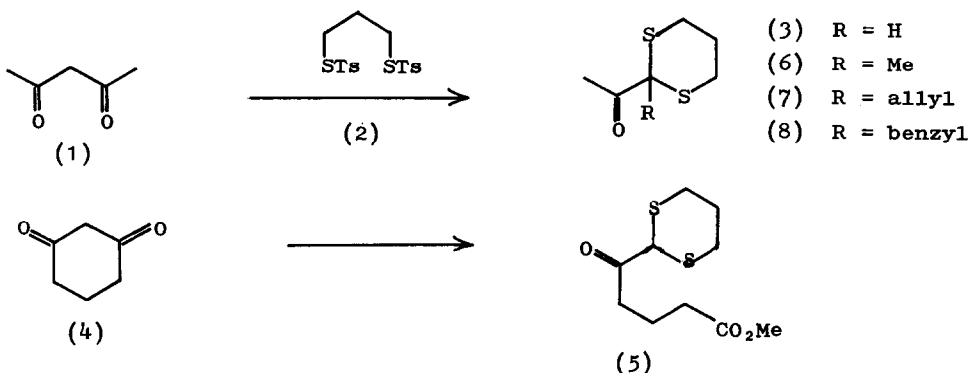
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A mild method for cleaving 1,3-diketones is described. The products are 2-acyldithianes and these $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}^{\ominus}$ synthons can be alkylated under mildly basic conditions.

Acetylacetone (1) reacted with propane-1,3-dithio tosylate (2) in methanol to give 2-acetyl-1,3-dithiane† (3) (82%), whose ¹H-n.m.r. spectrum showed a characteristic singlet at δ 4.05. Similar treatment of cyclohexane-1,3-dione (4) gave the keto-ester (5) (93%).

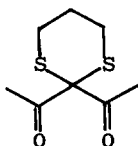


Unlike the products of the Woodward-Pachter reaction,¹ (3) and (5) are acidic 2-acyldithianes and can therefore be alkylated to afford protected 1,2-diketones. Thus (3) was converted to the methyl derivative (6) using

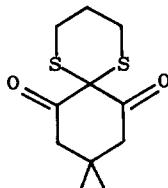
† Satisfactory microanalytical and spectral data were obtained for all compounds reported in this paper.

NaH/DMF/MeI, while reaction with allyl bromide or benzyl bromide in diethyl ketone/ K_2CO_3 , gave the corresponding derivatives (7) and (8).

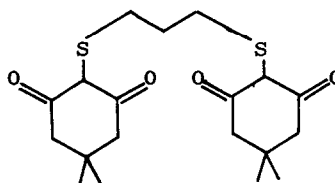
The intermediates in the cleavage reaction are presumably diacyl dithianes, and (9) was isolated (in 65% yield) by using the less nucleophilic solvent ButOH. Under the same conditions dimedone gave a mixture of (10) (42%), m.p. 128-129° and the 2:1 adduct (11) (46%), m.p. 158-161°, M^+ , 384.



(9)



(10)



(11)

Diacyl dithianes (e.g. 9, 10) may be useful intermediates for the otherwise difficult reduction² of acidic 1,3-diketones to 1,3-diols.

REFERENCES

1. R. B. Woodward, I. J. Pachter and M. L. Scheinbaum, J. Org. Chem., 1971, 36, 1137.
2. cf. J. Dale, J. Chem. Soc., 1961, 910.