

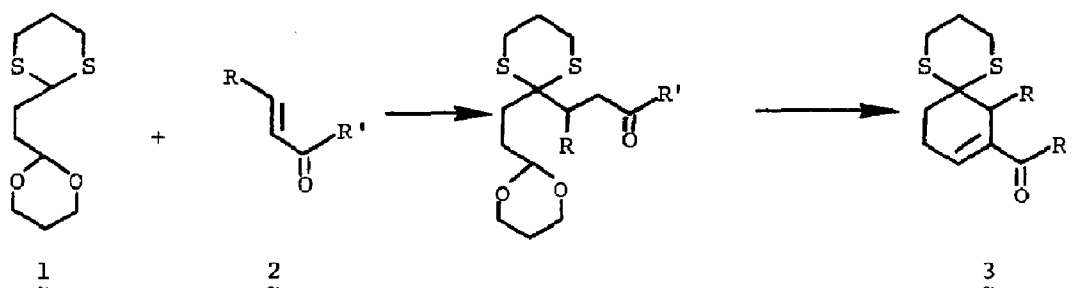
A REAGENT FOR CYCLOHEXENE ANNELATION

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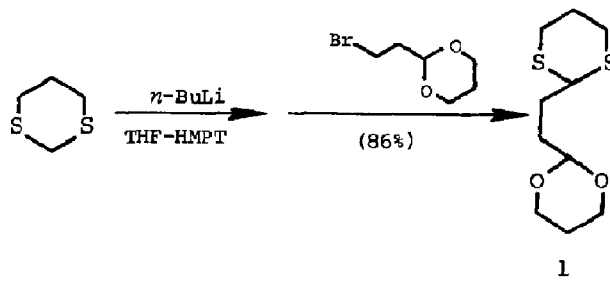
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Summary: Reagent 1 is a useful reagent for carrying out the annelation 2→3.

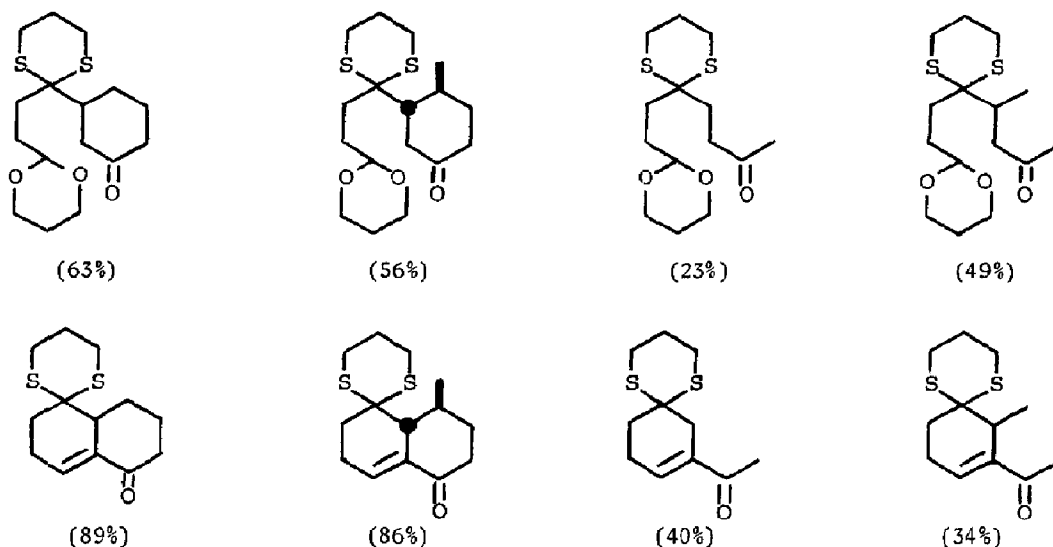
Brown and Yamaichi recently reported that alkyldithiane anions add to enones in a conjugate fashion when hexamethylphosphorous triamide (HMPT) is used as co-solvent.^{1,2} We have capitalized on this interesting observation to develop a reagent (1) which may be used to accomplish the following transformation:



Compound 1 (mp 59.5-60°) is prepared in 86% yield by alkylation of 1,3-dithiane with 2-(2-bromoethyl)-1,3-dioxane³ in THF containing 1.3 mol-equivalent of HMPT.



The anion of 1 is prepared as described by Brown and Yamaichi and added to the appropriate enone (-78° C, 1 eq of 1, 1 eq of *n*-BuLi, 1.9 eq HMPT, 1 eq of enone). The resulting addition product is hydrolyzed and cyclized by heating with HCl in aqueous methanol (1:10 10% HCl:CH₃OH) for several hours. The following adducts and annelation products have been prepared:



Although we have not attempted to optimize yields in all cases, it is clear that the cyclohexenones give fewer by-products than the acyclic enones studied. We have made a fairly thorough effort to optimize the yield of an adduct with methyl vinyl ketone (MVK) and have realized the indicated yield only by slow addition (syringe pump) of MVK to the solution of the anion of 1. Compound 1 does not undergo conjugate addition to enones which are completely substituted at the β -position (3-methylcyclopentenone, mesityl oxide).

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R E F E R E N C E S

1. C.A. Brown and A. Yamaichi, *J.C.S. Chem. Commun.*, 100 (1979).
2. For other recent examples of conjugate additions of dithiane anions to enones see (a) J. Lucchetti, W. Dumont and A. Krief, *Tetrahedron Lett.*, 2695 (1979); (b) F.E. Ziegler and C.C. Tam, *Tetrahedron Lett.*, 4717 (1979).
3. Prepared from acrolein, 1,3-propanediol, and HBr by the method of U. Faass and H. Hilgert *Chem. Ber.*, 87, 1343 (1954).

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