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TRANS-1-BUTADIENYLTRIPHENYLPHOSPHONIUM BROMIDE: A REAGENT FOR THE 1,3-CYCLOHEXADIENYLATION OF CARBONYL GROUPS.

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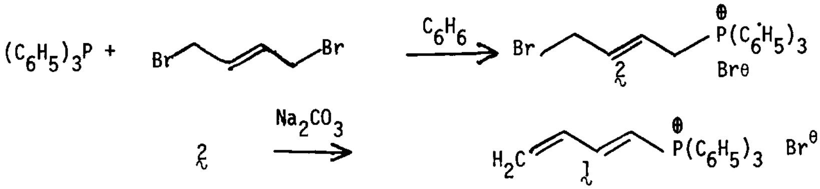
In connection with our interest in synthetic methodology stemming from conjugate addition--intramolecular Wittig reactions,[1] we have examined the reaction of enolates with trans-1-Butadienyltriphenylphosphonium bromide 1 and have found that this combination results in a facile one-step synthesis of substituted 1,3-cyclohexadienes.

Reagent 1[2] was easily prepared (92% overall, 0.5 mole scale) by reaction (RT, 18 hours, C_6H_6) of triphenylphosphine with trans-1,4-dibromobut-2-ene (Aldrich) and subsequent dehydrohalogenation of the resulting trans-4-Bromo-but-2-enyl-1-triphenylphosphonium bromide 2[3] with anhydrous sodium carbonate (3 eq., RT, $CHCl_3$, 18 hours).



Reaction of 1 (1.1 eq., THF, RT, 6-18 hours) with a representative sample of carbonyl compounds 3a-f (as their enolates[4]) produces 1,3-cyclohexadienes 4a-f in moderate yield.[5,6,7] (See Table I).

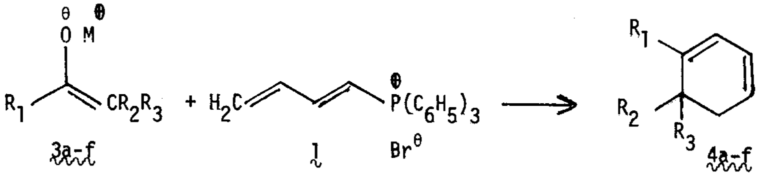
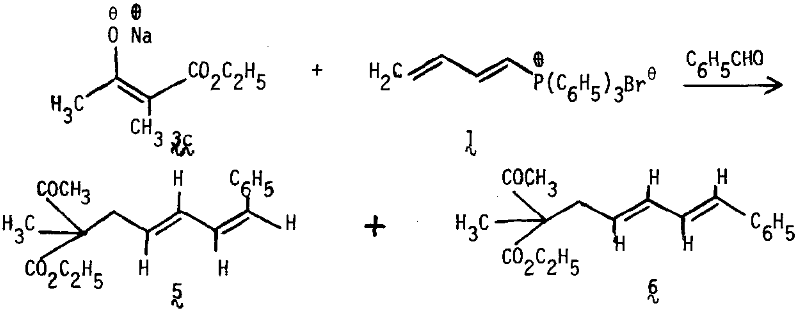


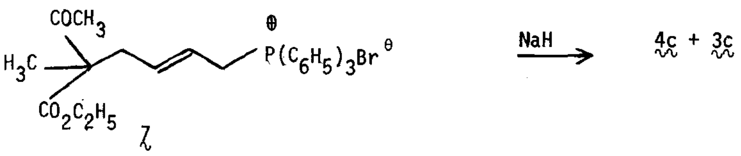
TABLE I

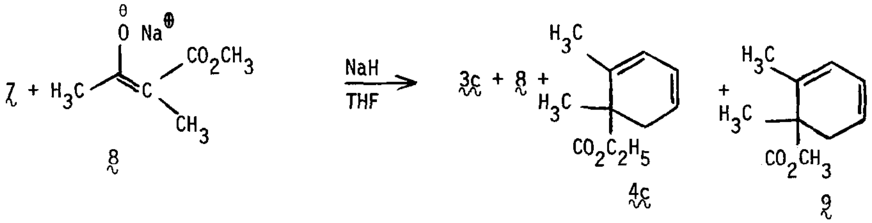
3	4 (yield)
a R_1=H, R_2=CH_3, R_3=$COCH_3$	35%
b R_1=R_2=CH_3, R_3=$COCH_3$	40%
c R_1=R_2=CH_3, R_3=$CO_2C_2H_5$	57%
d R_1=R_3=C_6H_5, R_2=H	57%
e R_1=C_6H_5, R_2=R_3=H	45%
f R_1=H, R_2=R_3=C_6H_5	35%

It should be noted that this procedure is a $C_4 + C_2$ synthesis of 1,3-cyclohexadienes, and as such, affords complementary substitution patterns to the $C_3 + C_3$ cyclohexadiene synthesis recently demonstrated to result from the reaction of allyl ylides and enones[8].

In an effort to elucidate the mechanism of cyclohexadiene formation, the following reactions were performed: Reaction of 3c with 1 in the presence of benzaldehyde (1.1 eq., RT, 0.5 hour) failed to produce cyclohexadiene 4c (<1%) but instead, yielded (72%) a 2:1 mixture of butadienes 5 and 6.[5,9,10] Reaction of allyl phosphonium salt 7[5,11] with sodium hydride (THF, RT, 18 hours) produced 4c (55%) and 3c (5%). Furthermore, repetition of the above experiment with the addition of the sodium enolate of 2-methylmethylacetoacetate 8 (1.1 eq.) produced a mixture of 4c (34%), 8 (26%), 3c (33%), and carbomethoxycyclohexadiene 9 (22%).

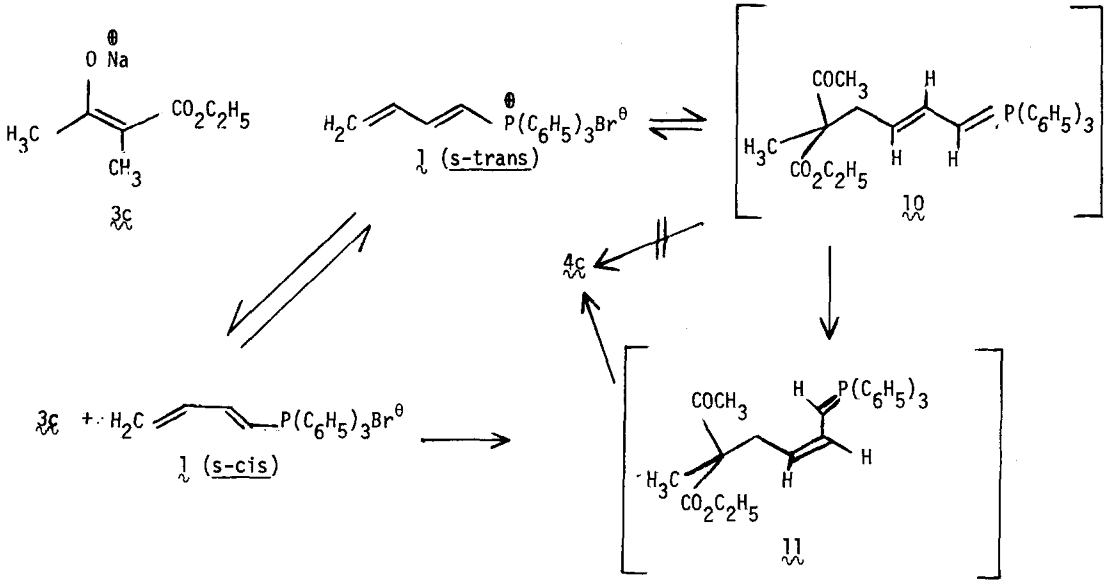






The above data can best be accomodated by the following scheme: Enolate addition to s-trans-1 produces trans-allyl ylide 10 (which is prevented from direct closure to 4c because of geometrical constraints) which can be trapped by benzaldehyde to give butadienes 5 and 6. In the absence of an external trap, 10 can revert to starting materials. Addition to s-cis-1 may directly generate cis-allyl ylide 11 which then closes to the observed product 4c.

The available data does not preclude slow, direct conversion and of 10 to 11 followed by ring closure to 4c.[12]



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FOOTNOTES

1. P.L. Fuchs, J. Amer. Chem. Soc. 96, 1607 (1974).

2. 1, MP 186-188.5°(from CHCl$_3$/ether), literature MP 182-184°[J.A. Ford, C.V. Wilson, J. Org. Chem. 26, 1433 (1961)]. Analysis: Found: 67.04%C, 4.86%H, 7.70%P, Calc: 66.85%C. 5.10%H, 7.84%P. 1 has been shown to have trans stereochemistry by heteronuclear spin decoupling experiments at 100 MHz.

3. E. Buchta, F. Andree, Ann. Chem. 640, 29, 1961.

4. Enolates 3a-c were prepared from the corresponding β-dicarbonyl compound (NaH, THF, RT). Enolates 3d-f were prepared by reaction of the corresponding carbonyl compound and Lithium Hexamethyldisilazane at -78°. [M.W. Rathke, J. Amer. Chem. Soc. 92, 3222, (1970)].

5. Structure assigned by IR, NMR, MS, and exact mass.

6. Small amounts (0-7%) of recovered 3a-f and triphenyl phosphine were also produced in this reaction. Yields refer to isolated material of > 95% purity.

7. Unsubstituted β-ketoesters or β-diketones fail to give acceptable yields of cyclohexadienes in this reaction.

8. (a) G. Büchi, H. Wüest, Helv. Chim. Acta., 54, 1767 (1971). (b) W.G. Dauben, D.J. Hart, J. Ipaktschi, A.P. Kozikowski, Tetrahedron Lett, 4425, (1973). (c) W.G. Dauben, A.P. Kozikowski, Tetrahedron Lett. 3711, (1973). (d) W.G. Dauben, J. Ipaktschi, J. Amer. Chem. Soc., 95, 5088 (1973). (e) F. Bohlman, C. Zedro, Chem Ber. 3779, (1973). (f) A. Padwa, L. Brodsky, J. Org. Chem. 39, 1318 (1974).

9. 5 and 6 were both shown to have trans-geometry about the internal double bond by proton decoupling. No olefin corresponding to 1,2-addition was observed.

10. Trapping of ylides produced by 1,4-addition to butadienylsulfonium salts has also been observed: (a) H. Braun, N. Mayer, G. Dresze, Ann. Chem. 762, 111 (1972). (b) H. Braun N. Mayer, G. Strobl, G. Kresze, Ann. Chem. 1973, 1317. (c) H. Braun, G. Huber, G. Kresze, Tetrahedron Lett, 4033 (1973).

11. 7, MP 148-150° (CHCl$_3$/ether), prepared from 3c via successive reactions with trans-1,4-dibromobut-2-ene (3 eq., THF/10%HMPA) and triphenylphosphine (C_6H_6, 3 hours, reflux). **Trans**-stereochemistry of 7 has been confirmed by proton decoupling.

12. The general question of trans→cis allyl ylide interconversion also bears on the C_3 + C_3 cyclohexadiene synthesis[8]. Experiments designed to evaluate this pathway will be reported on in due course.