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TANDEM ANNULATIONS.
2-BROMOMETHYL-3-(TRIMETHYLSILYLMETHYL)BUTA-1,3-DIENE AS A SYNTHON FOR A ZWITTERION OF 2,2'-BIALLYL

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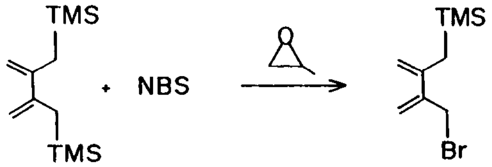
Summary: Alkylation of an enolate with the titled conjunctive reagent followed by cyclization of the allylsilane moiety onto the carbonyl group effects the first annulation; the resultant 2,3-dimethylene-cyclohexane participates in a subsequent Diels-Alder reaction to complete the second annulation.

Bifunctional conjunctive reagents that contain both nucleophilic and electrophilic centers whose reactivity is so adjusted to avoid self-annihilation offer the opportunity to create useful annulating agents.[1] Biallyl **1a**, a fascinating reactive intermediate,[2] offers the opportunity of multiple ring annulations since an initial product would be a 2,3-disubstituted-1,3-butadiene, an excellent diene for a Diels-Alder reaction.[3,4] We wish to report the synthesis of 2-bromomethyl-3-(trimethylsilylmethyl)-buta-1,3-diene (2), a synthon for a dipolar version of **1a**, i.e., **1b**, and its use in a tandem annulation.


1a

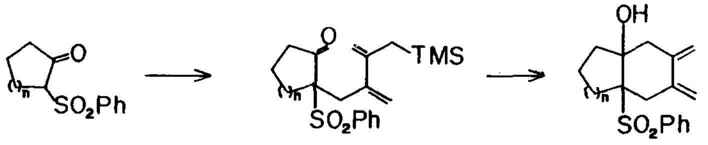

1b

Subjection of 2,3-bis(trimethylsilylmethyl)-buta-1,3-diene[4] to 1.15 eq of NBS in THF at -78° in the presence of propylene oxide gave the desired conjunctive reagent **2**[5] in 40-50% yield after chromatography as a delicate oil



2

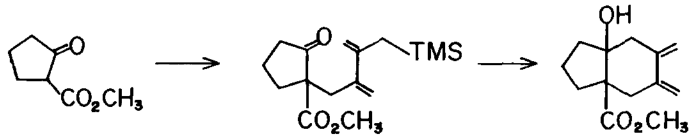
[IR 3110, 2970, 1595, 910, 885, 855. NMR δ0.0 (s, 9H), 1.8 (s, 2H), 4.2 (s, 2H), 5.0 (s, 1H), 5.2 (s, 1H), 5.3 (s, 1H), 5.42 (s, 1H)]. Alkylation of the ketosulfones 3 and **4** or β-ketoester **5** is best accomplished by treating their corresponding sodium or potassium salts (NaH or KH) with **2** in refluxing DME to give **6-8**[5] in 50-60% yields. Characteristic absorptions in the NMR spectrum appear at δ1.70±0.04 (s, C=C$\underline{CH}_2$TMS), δ2.64±0.11 and δ2.92±0.11 (AB, J=15Hz, C$\underline{H}_2$C=), δ4.77±0.05, 4.88±0.02, 4.94±0.02, and 5.18±0.06 (each s, =C-$\underline{H}$).



3 n=1
4 n=2

6 n=1
7 n=2

9 n=1
10 n=2

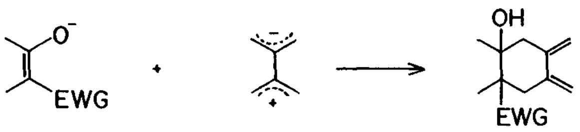


5

8

11

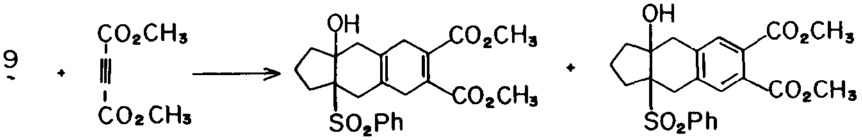
Cyclization to the 2,3-dimethylenecyclohexane occurs smoothly with either tetra-n-butylammonium fluoride (THF,55°)[6] or ethylaluminum dichloride (CH_2Cl_2, -78°)[7] to give **9-11**[5] in 60-78% yields, the latter reagent being preferred in the cyclization of **8** to **11**. Characteristic absorptions for the bis-methylene unit appear at δ4.73±0.02, 4.80±0.05, 5.17±0.13, and 5.20±0.15. This two step sequence constitutes the equivalent of adding the biallyl unit to an electron rich olefin as symbolized by eq 1.



(1)

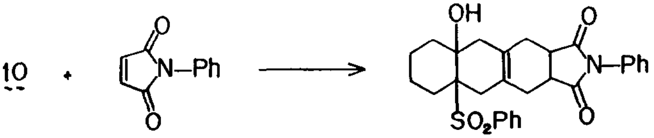
This formation of the dimethylenecyclohexane unit sets the stage for the second annulation, the Diels-Alder reaction. Dienes **9** and **10** cycloadded with dimethyl acetylenedicarboxylate (eq 2, 95%) and N-phenylmaleimide (eq 3, 66%)

respectively in refluxing THF. In the former case, the initial adduct **12** was contaminated by a small amount of its dehydrogenated product **13**. Diene **11** smoothly cycloadded with phenylvinyl sulfone[8] to give a regioisomeric mixture of adducts (eq 4, 80% yield). Chemoselective reductive desulfonylation with buffered sodium amalgam[9] gave the cyclopentano-1,2,3,4,5,6,7,8-octahydronaphthalene **15**[5] in 71% yield.

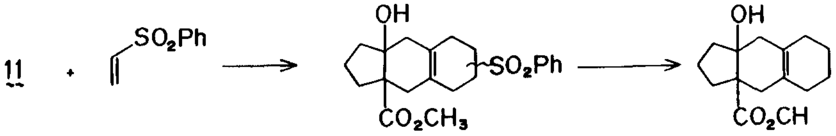


12 **13**

(2)



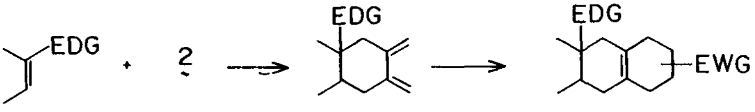
(3)



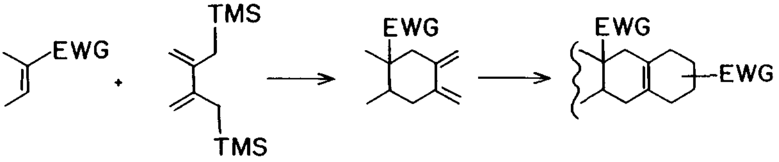
14 **15**

(4)

The ability to generate multiple ring systems rapidly improves access to many of the complex molecular systems that are common synthetic targets. Tandem annulation offers one such approach. With the availability of the conjunctive reagent 2, electron rich olefinic systems such as enolates (EDG - electron donating group) provide a ready access to bicycles according to eq 5.



(5)



(6)

This reagent offers an excellent complement to the recently reported sequence with 2,3-bis(trimethylsilylmethyl)buta-1,3-diene[4] which allows such an elaboration beginning with the electronically reversed situation, i.e., electron deficient olefins as in eq 6 (EWG - electron withdrawing group).

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