Bicycloannulation of Cyclohexenones with Vinyl and Isopropenyl Sulphones

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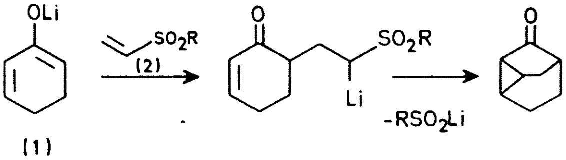
Summary Tricyclo[3.2.1.0^{2,7}]octan-6-ones are formed in one step from $\alpha\beta$-cyclohexenones by treatment of their α'-enolates with vinyl and isopropenyl phenyl sulphones in the presence of hexamethylphosphoric triamide.

VINYLPHOSPHONIUM bicycloannulation of $\alpha\beta$-cyclohexenones has been demonstrated to be an efficient method for the synthesis of substituted tricyclo[3.2.1.0^{2,7}]octan-6-ones, which have served as important intermediates in a variety of synthetic contexts.[1] The success of this process depends to a great extent upon the ability of the phosphonium group to act both as an electron-withdrawing group and as a leaving group.

By analogy, reaction between the α'-enolate (**1**) of cyclohex-2-enone and a vinyl sulphone (**2**) might be expected to involve initial conjugate addition to the sulphone followed by intramolecular cyclopropanation of the enone moiety, as shown in Scheme 1. This type of conjugate addition and subsequent cyclization, but *without* loss of the sulphone group, has been utilized in alkaloid synthesis,[2] and base-catalysed intermolecular cyclopropanation of $\alpha\beta$-unsaturated esters by allylic sulphones has been in use for some time.[3] We now report that vinyl and isopropenyl phenyl sulphones provide variable yields of substituted tricyclo[3.2.1.0^{2,7}]octan-6-ones as in Scheme 1, provided hexamethylphosphoric triamide (HMPA) is added as co-solvent.†



SCHEME 1. Vinyl sulphone bicycloannulation.

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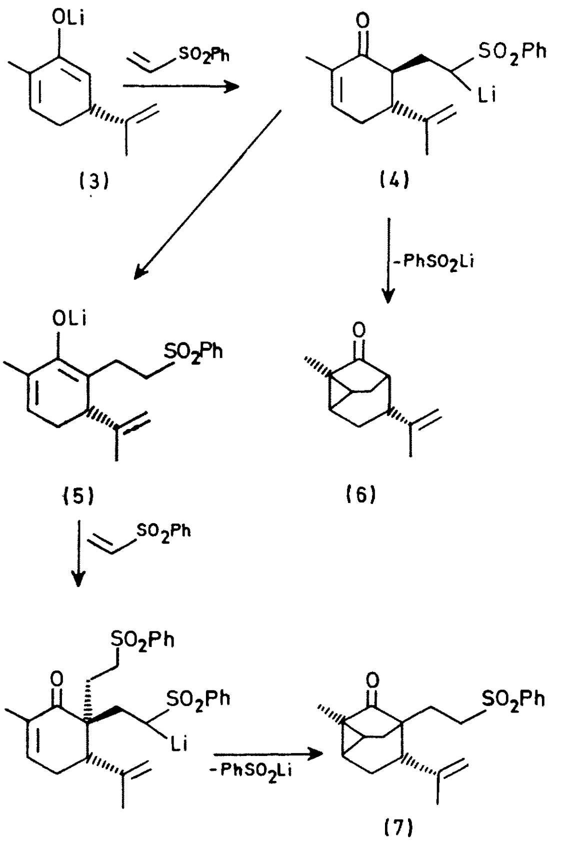
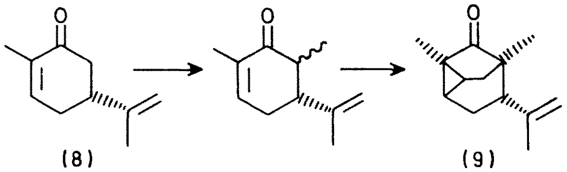
† No bicycloannulation products could be isolated in the absence of HMPA, in marked contrast to vinylphosphonium bicycloannulation, in which addition of HMPA had no effect.

Addition of phenyl vinyl sulphone (**2**, R = Ph) to a solution of the α′-enolate‡ (**3**) from (−)-carvone in THF (tetrahydrofuran) containing HMPA (4 : 1 mol ratio of HMPA to ketone) at room temperature, followed by refluxing, gave a disappointingly low yield (5%) of the desired tricyclo-octanone (**6**),[1] along with a small amount of another bicycloannulation product (**7**), presumably formed *via* proton transfer involving the sulphonyl carbanion precursor (**4**), giving the more stable α′-enolate (**5**) which is itself then bicycloannulated by a second molecule of the vinyl sulphone (Scheme 2). Methylation§ of (−)-carvone (**8**) prior to bicycloannulation eliminated this side reaction and led to a higher yield (17%) of the desired product (**9**).¶

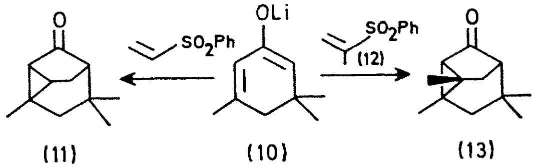


SCHEME 2. Bicycloannulation of (−)-carvone.

All the above-mentioned products (**6**), (**7**), and (**9**) were formed stereoselectively by attack of the sulphone on the less hindered side of the enolate.



Surprisingly, when the α′-enolate (**10**) from isophorone was treated under the same conditions with the same vinyl sulphone, a 38% yield of the expected tricyclo-octanone (**11**) was obtained. Although a considerable amount of starting ketone was recovered (47%) in this case, no product analogous to the 2 : 1 condensate (**7**) could be isolated. The yield of ketone was, in fact, four times greater than the yield of the same compound from vinylphosphonium bicycloannulation,[1] indicating that these two methods may be complementary to each other. Similarly, use of isopropenyl phenyl sulphone (**12**) with the same substrate produced a 21% yield of tricyclo-octanone (**13**).¶ Interestingly, the latter reaction proceeded at room temperature, whereas the corresponding vinyl sulphone required refluxing before any significant formation of tricyclo-octanone was observed.



Since the sulphones are soluble in THF, they are more convenient to use than the phosphonium salts. Furthermore, the ready availability of vinyl and other αβ-unsaturated sulphones having a variety of substituents in place of phenyl allows their reactivity to be varied over a wide range, and we are actively investigating this aspect.

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‡ Formed by slow addition of the ketone to excess of LDA (lithium di-isopropylamide) in THF at 0 °C.

§ LDA, 0 °C; methyl iodide.

¶ Satisfactory ^{1}H and ^{13}C n.m.r., i.r., and mass spectra (including the precise mass of the molecular ion) were obtained.

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