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Unusual [8 + 2] Annelation in the Reactions of Allenic Ester/Ketone-Derived 1,3-Dipoles with Tropone

Kamal Kumar, Ashish Kapur, and Mohan Paul S. Ishar*

Department of Pharmaceutical Sciences, Guru Nanak Dev University,
Amritsar-143 005, Punjab, India

mpsishar@angelfire.com

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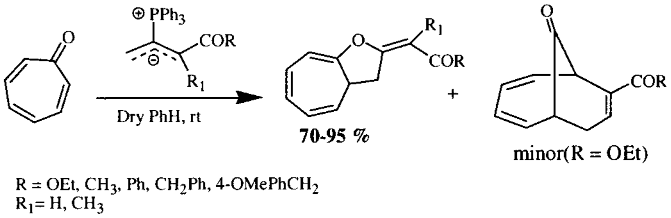
ABSTRACT

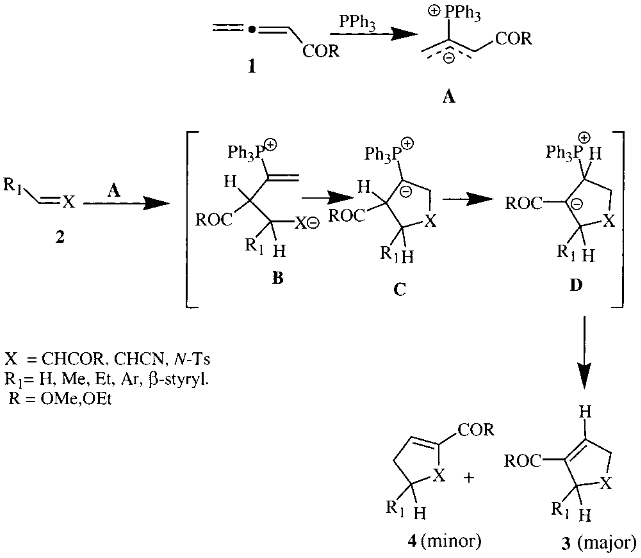


All-carbon 1,3-dipoles derived from allenic esters/ketones, by catalytic interaction with triphenylphosphine, undergo an unusual [8 + 2] annelation with tropone, leading to 8-oxa-9-(ethoxycarbonyl/acylalkylidene)bicyclo[5.3.0]deca-1,3,5-trienes. Dipoles derived from allenic ketones as well as an α-methyl-substituted allenic ester display high reactivity and selectivity.

Since the first publication on phosphine-catalyzed dipolar addition of an allenic ester to electron-deficient olefins,[1] a number of reports describing addition of the all-carbon 1,3-dipole **A**, derived from the interaction of phosphines with allenic esters or butynoates, to a variety of polarized/reactive π-systems have appeared in the literature.[2] The generally accepted stepwise mode of addition involving a series of intermediates (**B** → **C**→ **D**) is outlined in Scheme 1. However, an alternative concerted initial addition leading directly to **C** has not been ruled out.[2b] The addition has been reported to be regioselective, yielding mainly **3**; however, the other regioisomer (**4**) has been obtained as a minor product in most of the reactions.

Cycloadditions of dipole **A** with tropone were of particular interest due to the diverse periselectivities displayed by the latter.[3] In general, difficulties are associated with predicting the periselectivities in cycloadditions involving tropone and fulvenes.[3,4] For instance, the rationalization of the dichotomy observed in 1,3-dipolar cycloadditions to fulvene is based

Scheme 1



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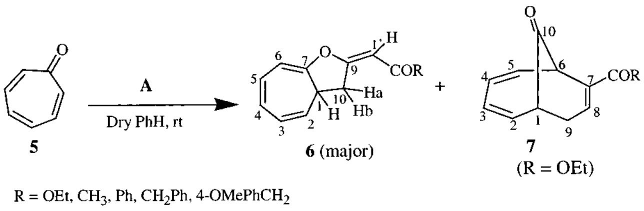
on involved mechanistic postulations.[5] In a continuation of our investigations on thermal cycloadditions involving tropone and allenic systems,[3] we have investigated the cycloadditions of tropone (**5**) with dipoles **A** derived from allenic ester/ketones **1**. For the first time the dipoles have been generated from allenic ketones and used successfully in annelation. The results in Scheme 2 and Table 1 are highly unexpected as only regioselectively formed (8 + 2) cycloadducts **6a**−**e** are obtained in very high yields and formation of any (2 + 3) addition product is not observed; (6 + 4) cycloadduct **7a** has been isolated only in the case of allenic ester **1a** as a minor product. The reactions were fast and occurred at ambient temperature, and even lowering the temperature to 0 °C did not affect either reaction time or yield.

Scheme 2



Compounds **6a**−**e** and **7a** have been characterized by spectroscopic analysis (IR, ^{1}H NMR, ^{13}C NMR, and mass) and elemental analysis. The characteristic feature of the ^{13}C NMR spectrum of **6a** was the presence of two upfield shifted olefinic carbons (CH) at δ 93.38 and 98.85 (C1′ and C6) and two downfield shifted quaternary olefinic carbons at δ 173.25 (C9) and 150.31 (C7); the ^{13}C NMR resonance for the tropone carbonyl was absent. The regiochemistry of addition is based on the ^{1}H NMR chemical shift of C10-Hs and the presence of their vicinal couplings with C1-H. Similar structural conclusions could be drawn for other (8 + 2) cycloadducts. The indicated geometry at the exocyclic double bond in **6a**−**e** is based, interalia, on the absence of any close spatial proximity between C1′-H and C10-Hs (absence of ^{1}H NOE). The structural assignments of the (6 + 4) cycloadduct was rather straightforward.[6]

Table 1. Reaction of Tropone with Dipole **A** Derived from Allenic Esters/Ketones

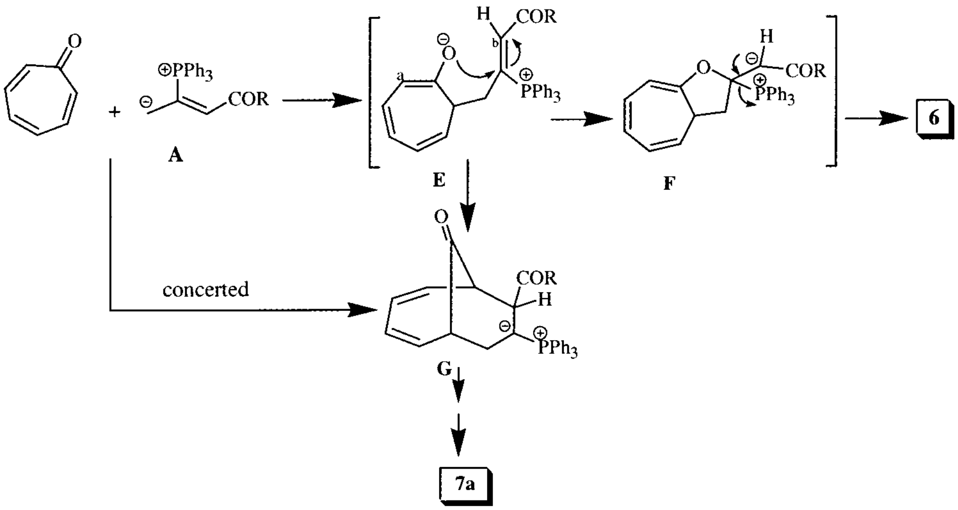
no.	R	reactn time[a] (h)	product (% yield)	
1	OEt	3.5	**6a** (82)	**7a** (14)
2	Me	3.0	**6b** (95)	nil
3	Ph	5.0	**6c** (90)	nil
4	CH_2Ph	8.0	**6d** (90)	nil
5	CH_2Ph-*p*-OMe	6.0	**6e** (90)	nil

[a] Reactions performed at ambient temperature.

The present results are in sharp contrast not only to the reported behavior of dipole **A** (Scheme 1) but also to the reported 1,3-dipolar cycloadditions to tropone. The latter additions have been reported to yield mainly (2 + 3) cycloadducts, and occasionally (4 + 6) adducts have been obtained as minor products.[7] On the other hand tropone has been reported to yield (8 + 2) cycloadducts on reaction with tetracarbethoxyallene and phenylsulfonylallene in refluxing benzene;[8] however, it mainly yields a number of (4 + 2) cycloadducts with a variety of ethyl 2,3-dienoates, in low yield.[3]

Mechanistically, the regioselective formation of (8 + 2) cycloadducts can be rationalized in terms of an initial frontier controlled[9] attack of C3 of the dipole (an allyl anion)[4] at C2 (having largest coefficient in the LUMO) of tropone,[4c] leading to **E**, which is followed by nucleophilic attack of the negatively charged oxygen at the central carbon of the dipole with consequent elimination of phosphine, leading to **6** (Scheme 3). The (6 + 4) adduct **7a** may have been derived from **E** by nucleophilic attack of atom a on b leading to **G**, followed by the same general steps as shown in Scheme 1;

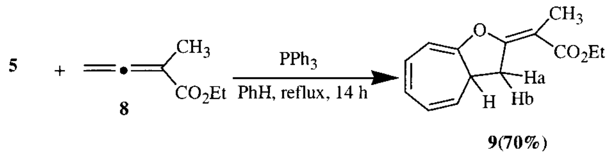
Scheme 3



alternatively **7a** could result from a concerted initial addition leading to **G**.

To substantiate the mechanistic postulations,[10] the reaction has been extended to ethyl 2-methylbuta-2,3-dienoate (**8**) which also underwent triphenylphosphine-catalyzed addition to tropone, albeit, at higher temperature, to afford **9** in 70% yield (Scheme 4); a single geometric isomer involving the exocyclic double bond is obtained and the assigned geometry is based on analogy with that of **6a**−**e**.

Scheme 4



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Supporting Information Available: Experimental procedures and full characterization for compounds **6a**, **6b**, **7a**, and **9**; IR and ^1H NMR spectrum of **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Cantrell, T. S. *Tetrahedron Lett*. **1975**, 907. (b) Salem, L. *J. Am. Chem. Soc*. **1968**, *90*, 543. (c) The invoking of frontier-controlled addition is necessitated by the observed regiochemistry of addition as the less negatively charged end of the dipole **A** is involved in attack on C2 of tropone, which is in sharp contrast to the reported preferred regiochemistry of addition of dipole **A** to various olefins as described in Scheme 1.[1,2] Also the presently obtained regiochemistry of [8 + 2] addition is opposite of what has been obtained in thermal (high temperature) addition of tropone to electron-withdrawing substitutents bearing allenes.[3,8b]

(10) In the case of **8** the electronic influence of the 2-methyl group was anticipated to retard both the formation of **A** and the cyclization step (**E** → **F**, Scheme 3) by diminishing the electrophilicity of the central allenic carbon. Consequently, the reaction in the case of **8** occurred only at elevated temperatures. Also, as anticipated, the dipole derived from allenic ester **8** did not yield any (6 + 4) cycloadduct.