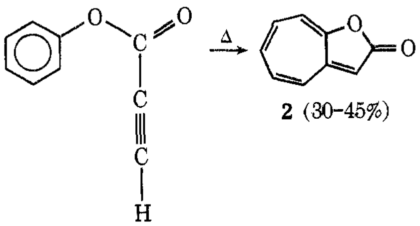
Communications

Formation of Tropolone Derivatives (2*H*-Cyclohepta[*b*]furan-2-ones) by the Pyrolysis of Aryl Propiolates

Summary: The flash vacuum pyrolysis of several aryl propiolates gives a 30–45% yield of various 2*H*-cyclohepta[*b*]-furan-2-ones; this reaction thus provides a method for converting phenols to cycloheptane derivatives.

Sir: A few years ago we reported that the flash vacuum pyrolysis (FVP) of phenyl propargyl ether at 460 °C gives substantial yields of 2-indanone (26%) and 1,2-dihydrobenzocyclobutene (31%).[1] The mechanism for the formation of 2-indanone was shown to involve a number of steps which results in a major but well-defined reorganization of atoms.

As an extension of this study we pyrolyzed phenyl propiolate (1).[2,3] Surprisingly, the FVP of 1, carried out at 650 °C and ~10^{-4} Torr as previously described,[4] did not give the expected products analogous to those obtained from the ether but gave instead a fair yield of the tropolone derivative 2*H*-cyclohepta[*b*]furan-2-one (2). Lactone 2[5] and substituted ones[6] have been synthesized from 2-chlorotropone and have been converted to a number of cycloheptane derivatives including 2-methyltropone[5] and substituted azulenes.[7] Thus the preparation of 2 from 1 provides the basis for a general procedure for converting phenols to cycloheptane derivatives.



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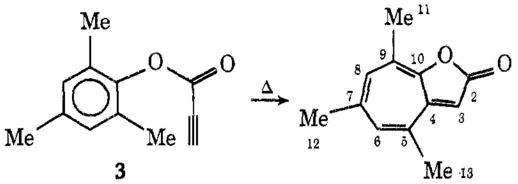
2 (30–45%)

Pyrolysis[4] of 2,4,6-trimethylphenyl propiolate (3) (mp 57–58 °C)[2,8] gave a 45–50% yield of 4 (mp 185–186 °C dec): ir (CCl$_4$) 1765, 1508, 1239 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.90 (s, 1 H), 6.78 (s, 1 H), 5.58 (s, 1 H, H$_3$), 2.42 (s, 3 H), 2.33 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 168.84 (C$_2$), 151.36 (C$_4$ and C$_{10}$), 139.08, 137.58, 137.06, 133.94, and 125.17 (C$_5$ to C$_9$), 95.42 (C$_3$), 27.39 (C$_{12}$, q, $J_{\text{C-H}}$ = 128.0 Hz, of t, $J_{\text{C-H}}$ = 6 Hz), 24.27 (q, $J_{\text{C-H}}$ = 128.0 Hz, of d, $J_{\text{C-H}}$ = 7.4 Hz) and 19.72 (q, $J_{\text{C-H}}$ = 129.4 Hz, of d, $J_{\text{C-H}}$ = 5.9 Hz) (C$_{11}$ and C$_{13}$).[9] The ^{1}H NMR signal at δ 5.58 indicates that the three methyl groups are on the seven-membered ring. Long-range proton coupling to the carbon atoms of the methyl groups was used to assign their positions.[10] Two of the methyl group quartets were split into doublets and one of them was split into a triplet. Only the distribution of methyl groups shown will account for these long-range splittings.



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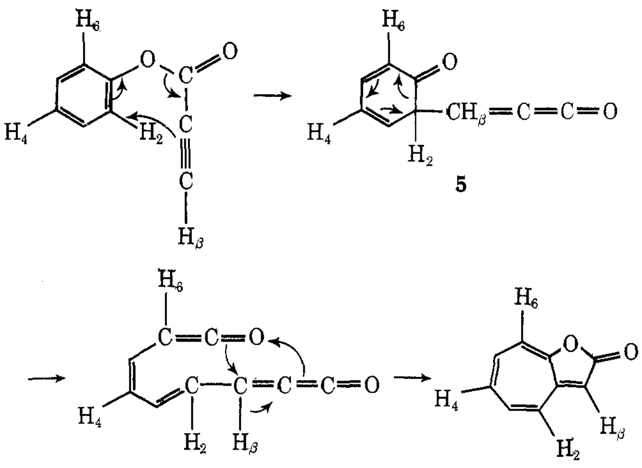
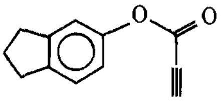
4 (45–50%)

The mechanism shown in Scheme I accounts for the positions of the methyl groups of 4. The formation of intermediate 5 by a Claisen-type rearrangement is reasonable even for acetylenic systems[1,11] and methylene ketenes have been observed recently.[12] The sequence of atoms of intermediate 5 is the same as that of the product (7) except for the position of H$_\beta$. Several reasonable pathways leading from 5 to 7 can be written and the one shown is presented simply to indicate the overall bond changes.

Scheme I



Also consistent with the mechanism shown in Scheme I is the observation that the FVP of 8 (mp 69–70 °C)[2,8] gave a 20% yield of 9 and a 20% yield of 10. Lactones 9 and 10 were separated by thick layer chromatography using multiple elutions with 25% ethyl acetate in hexane.



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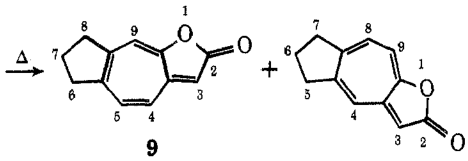


9

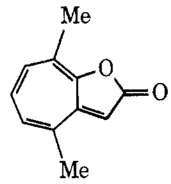
10

Lactone 9: more rapidly moving; mp 118–123 °C dec; ir (CHCl$_3$), 1750, 1615, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.13 and 7.00 (AB pattern, J_{AB} = 11 Hz), 6.95 (m, 1 H), 5.65 (m, 1 H), 3.0 (m, 4 H), 2.0 (m, 2 H).[9]

Lactone 10: less rapidly moving; mp 96–98 °C dec; ir (CHCl$_3$) 1750, 1600, 1520, cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.28 (br s, 1 H), 6.9 (br s, 2 H), 5.60 (s, 1 H), 2.95 (m, 4 H), 2.0 (m, 2 H).[9]

Structure 9 is assigned to the isomer with the low field AB pattern and structure 10 is assigned to the other one with a singlet at δ 7.28 since the following results establish that the ^{1}H NMR signals at *ca.* δ 7.2 are due to the H$_4$ protons.

The ^{1}H NMR spectra of 4 and 11,[8] which was prepared from the FVP of 2,6-dimethylphenyl propiolate,[2,8] show no signal at *ca.* δ 7.2 and therefore the signals at about δ 7.2 for 9 and 10 must result from the H$_4$ or H$_9$ protons. In an effort to assign these signals to either the H$_4$ or H$_9$ protons, lactones 12 and 13 were prepared in 50–60% yield by the FVP of *o*-methylphenyl propiolate (14).[2,8] The isomeric lactones were obtained



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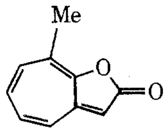

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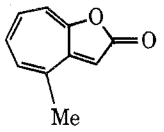

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in a 3:1 ratio and were separated by column chromatography. The major isomer [mp 116–117 °C; NMR (CDCl$_3$) δ 7.40–6.70 (m, 4 H), 5.70 (s, 1 H), 2.43 (s, 3 H); ir (CHCl$_3$) 1740, 1600, 1500, 1265 cm^{-1}][9] was assigned structure **12** because hydrolysis to the acid and decarboxylation of the acid, using a modification of Seto's method,[5] gave 2,7-dimethyltropone[13] [NMR (CDCl$_3$) δ 7.40–6.65 (m, 4 H), 2.30 (s, 6 H); ir (CHCl$_3$) 2980, 1620, 1570, 1365, 1150 cm^{-1}]. The minor isomer **13** [mp 116–116.5 °C (lit.[14] mp 116.5–117.5 °C); NMR (CDCl$_3$) δ 7.21–6.67 (m, 4 H), 5.68 (s, 1 H), 2.39 (s, 3 H); ir (CHCl$_3$) 1750, 1595, 1495, 1260 cm^{-1}][9] gave 2,3-dimethyltropone [mp 59–60 °C (lit.[14] mp 58–59 °C); NMR (CDCl$_3$) δ 7.08–6.67 (m, 4 H), 2.31 (s, 3 H), 2.21 (s, 3 H); ir (CHCl$_3$) 2980, 1630, 1560, 1470, 1365, 1110 cm^{-1}] when submitted to the hydrolysis-decarboxylation procedure. The NMR spectral data of **12** and **13** establish that the signals from **9** and **10** which are shifted slightly downfield from those for the other seven-membered-ring protons result from the H_4 protons.

The comparable yields of **9** and **10** indicate that the fused ring of **8** does not significantly affect the direction of the initial Claisen rearrangement and that both pathways are equally facile. However, the 3:1 ratio of **12** to **13** observed in the FVP of **14** most likely results from a steric effect of the *o*-methyl group.

The production of **10** is especially significant since it possesses the ring system of several guaianolides and pseudoguaianolides, two important classes of sesquiterpene hydroazulenic lactones.[15]

It is not clear why the pyrolysis of aryl propiolates gives different products from those obtained from the pyrolysis of aryl propargyl ethers.[1] It should be noted, however, that the pyrolysis temperatures for the esters are ~200 °C higher than those for the ethers and this temperature difference could be an important factor in accounting for the different reaction pathways.

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References and Notes

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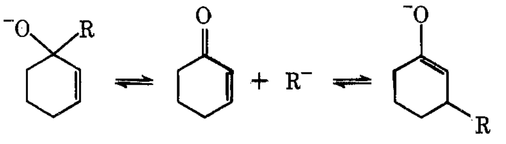
Conjugate and Direct Addition of Ester Enolates to Cyclohexenone. Selective Control of Reaction Composition

Summary: Direct addition of ester enolates to 2-cyclohexen-1-one at −78 °C is reversible at higher temperatures to give products of conjugate addition.

Sir: Reactions of stabilized carbanions with α,β-unsaturated carbonyl systems have received considerable attention during the past decade. Both 1,2 and 1,4 additions have been realized with conjugated enones. For example, dithianes undergo exclusive 1,2 addition;[1] anions of protected cyanohydrins give mixtures of 1,2- and 1,4-addition products.[2] Thioacetal monosulfoxides derived from formaldehyde undergo 1,2 addition; however, higher homologues give predominately 1,4 addition.[3] Although these reactions have been developed into important synthetic methodology, experiments which clearly identify the requirements of direct and conjugate addition have not been described. We wish to communicate our findings concerning reaction of ester enolates with 2-cyclohexen-1-one which, for the first time, demonstrate the importance of experimental parameters in partitioning direct and conjugate addition with stabilized carbanions.

At the outset of our work with ester enolate addition to enones, we had reason to believe that an equilibrium might be established between direct and conjugate addition products (eq 1).[4] Furthermore, we felt that, if kinetic addition occurs at the carbonyl carbon atom and equilibration leads to conjugate addition, then selective product formation might be possible by careful control of reaction temperature. As the following experiments demonstrate, this is indeed the case for reaction of ester enolates with 2-cyclohexen-1-one.



(1)

The ester enolate of methyl-2-phenoxypropionate (**1a**) is generated by addition of a tetrahydrofuran (THF) solution of **1a** to 1 equiv of lithium diisopropylamide (LDA), prepared in the usual manner[5] in THF at −78 °C. Addition of 1 equiv of 2-cyclohexen-1-one and stirring for 30 min, followed by careful quenching with saturated ammonium chloride solution at −78 °C, gives allylic alcohol **2a** (89% yield) and ketone **3a** (7%, bp 142–146 °C at 0.07 mm).[6] On the other hand, if the reaction mixture is warmed to 25 °C before quenching with water, ketone **3a** is the major reaction product (84% distilled yield). When a solution of pure **2a** (isolated as an oil by preparative, medium pressure, liquid chromatography) is added to 1 equiv of LDA at −78 °C and then is warmed to 25 °C, **3a** can be isolated in 91% yield.