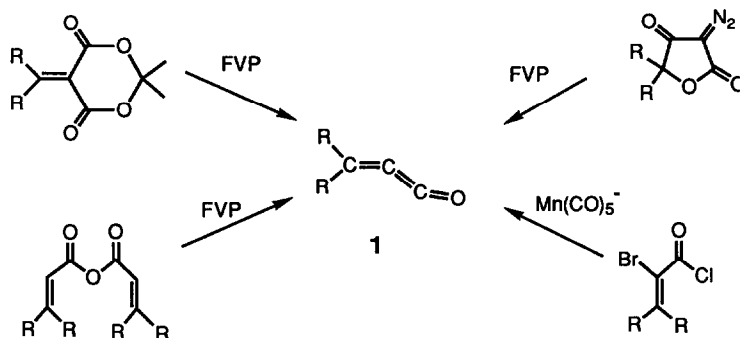


FLASH VACUUM PYROLYSIS OF 2-DIAZO-8-OXABICYCLO[3.2.1]OCT-6-EN-3-ONES. A NEW METHOD FOR THE PREPARATION OF PROPADIENONES.

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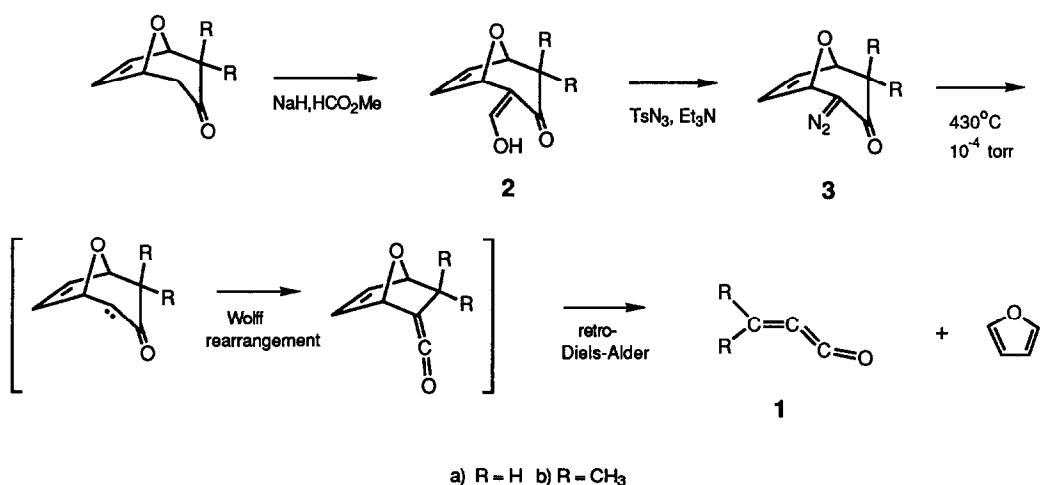
Summary: When diazoketones **3a** and **3b** are pyrolysed at 430°C and 10⁻⁴ torr, they undergo loss of N₂ followed by Wolff rearrangement and loss of furan by retro Diels-Alder reaction to yield the desired propadienones **1(a,b)**. If argon is added to the pyrolysate mixture, these reactive compounds can be trapped under matrix isolation conditions at 22 K and observed by FTIR. Upon photolysis, **1b** yields carbon monoxide and 2-butyne.

Because of their unusual bent geometries, high reactivities, and potential utility as photochemical sources of vinylidenes, propadienones (methyleneketenes) are of considerable theoretical interest.¹ In addition, they have also been shown to be useful synthetic intermediates.² Over the past two decades, several methods³ have been developed for the preparation of propadienones in the gas phase and in solution. The gas phase preparations involve flash vacuum pyrolysis (FVP) of appropriate precursors. In favorable cases these methods can be used to observe propadienones under matrix isolation conditions.^{3d} While all of these methods have certain advantages, none is a truly general method for the preparation of a wide variety of propadienones.



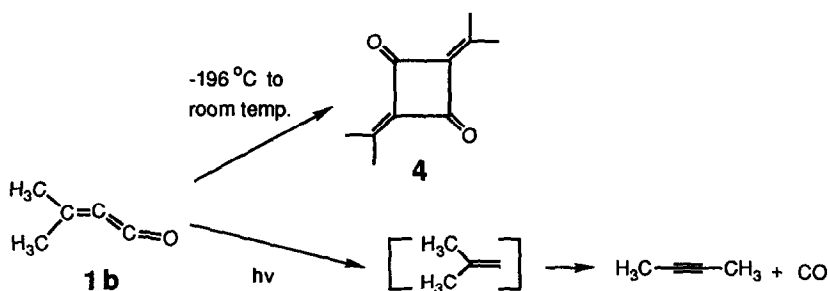
We have developed an alternative, potentially general method by which propadienones can be cleanly and conveniently generated under mild FVP conditions with only nitrogen and furan as byproducts. Our approach, illustrated by the preparation of propadienone (**1a**) and dimethylpropadienone (**1b**), starts with 8-oxabicyclo[3.2.1]oct-6-en-3-ones which are conveniently available from the [3+4] cycloaddition reaction of furan

with α,α' -dibromoketones in the presence of zinc.⁴ Conversion of the ketones to the hydroxymethylene compounds (NaH, HCO₂Et, EtOH)⁵ **2a** (mp 62-64 °C) and **2b** (mp 65-67 °C) occurs in 75% yield. Treatment of compounds **2a** and **2b** under standard conditions (TsN₃, Et₃N, CH₂Cl₂, -10°C)⁶ produces the diazoketones **3a** and **3b**, respectively. **3a** : 41% yield, mp 65-67°C. IR: 2080, 1650 cm⁻¹. ¹H NMR: δ 2.16 (d, J = 17.9 Hz, 1H), 2.77 (dd, J = 6.0, 17.9 Hz, 1H), 5.02 (dd, J = 1.6, 6.0 Hz, 1H), 5.51 (d, J = 1.7 Hz, 1H), 6.29 (dd, J = 1.9, 5.9 Hz, 1H), 6.50 (dd, J = 1.5, 5.9 Hz, 1H). ¹³C NMR: δ 39.0, 66.3, 74.7, 77.7, 132.9, 134.2, 189.4. HR-MS: (M + H⁺) 151.053, calcd for C₇H₇O₂N₂ 151.051. **3b**: mp 59°C (dec). IR: 2080, 1640 cm⁻¹. ¹H NMR: δ 1.01 (s 3H), 1.35 (s, 3H), 4.51 (d, J = 1.8 Hz, 1H), 5.42 (d, J = 1.7 Hz 1H), 6.34 (dd, J = 1.8, 5.9 Hz, 1H), 6.58 (dd, J = 1.7, 5.9 Hz 1H). ¹³C NMR: δ 20.0, 27.0, 47.2, 64.5, 75.2, 87.3, 132.1, 135.7, 196.7. HR-MS: (M+) 178.0741 calcd for C₉H₁₀N₂O₂ 178.0742. Elemental analysis: calc 60.67% C, 5.62% H; found 60.21% C, 5.69% H. When treated under FVP conditions, diazoketones **3** undergo loss of nitrogen and Wolff rearrangement to the corresponding ketene which subsequently undergoes loss of furan via retro Diels-Alder reaction and yields the desired propadienone **1**.



Thus, when diazoketone **3b** is sublimed through a tube heated to 430°C at 10⁻⁴ torr and the pyrolysate is collected in a -196°C trap, a mixture of furan and the known dimer of dimethylpropadienone⁷ (**4**) are observed in a 2:1 ratio as the only products. The parent propadienone does not yield a stable dimer, only polymer.^{3d} Treatment of either **3a** or **3b** under FVP conditions in a stream of argon or nitrogen at a pressure of 10⁻⁴ torr and collection of the pyrolysate mixture on a CsI plate cooled to 22 K yields a matrix of furan and the corresponding

propadienone which can be observed by FTIR. The major spectral lines can be assigned to the propadienones (1a,b) and furan and are consistent with literature values in the case of the parent compound.^{3d} The observed spectrum for dimethylpropadienone (2115, 2111, 1777, 1765, 1362 cm^{-1}) is consistent with the 2100 cm^{-1} band previously reported.⁷ Photolysis of matrix isolated dimethylpropadienone using a medium pressure mercury lamp through a Vycor filter results in the formation of 2-butyne and carbon monoxide as well as the photolysis products of furan. The decarbonylation reaction presumably proceeds through dimethylvinylidene. Similar photolysis of propadienone is reported to yield only acetylene and carbon monoxide.^{3d}



Ab initio calculations⁸ were performed for dimethylpropadienone at the HF/6-31G* level with complete geometry optimization.⁹ As is the case for the parent compound,¹⁰ analytical frequency calculations predict that the molecule will maintain C_{2v} symmetry. Experimentally, however, the heavy atom chain for these molecules is badly bent and this result can be successfully reproduced if electron correlation is included in the wavefunction.^{1e, 1f} Recently we reported¹⁰ that HF/6-31G* calculations correctly predict¹¹ that difluoropropadienone is badly bent. We have since investigated¹² several other monosubstituted propadienones and have found that when the heavy atom carbon chain is substituted by a single electronegative group such as fluorine, chlorine, hydroxy and amino, it is also predicted to be badly bent at the HF/6-31G* level.

In conclusion, we have demonstrated that the flash vacuum pyrolysis of the easily accessible diazo-8-oxabicyclo[3.2.1]-oct-6-en-3-ones (3a,b) results in the clean formation of propadienones. Extension of this methodology to the formation of other propadienones, either by variation of the starting dibromoketone or by alkylation of 2a, is underway.

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