

3(2H)-Furanones from Mercuric Acetate Oxidation
of Allenic Ketones. A Synthesis of Bullatenone

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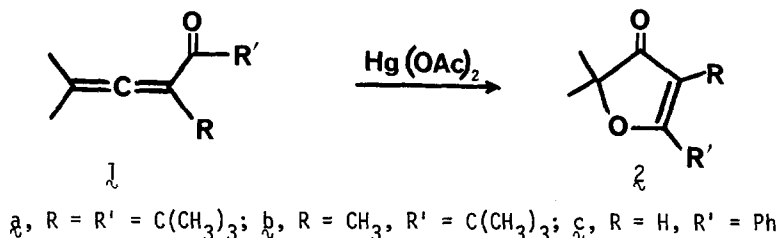
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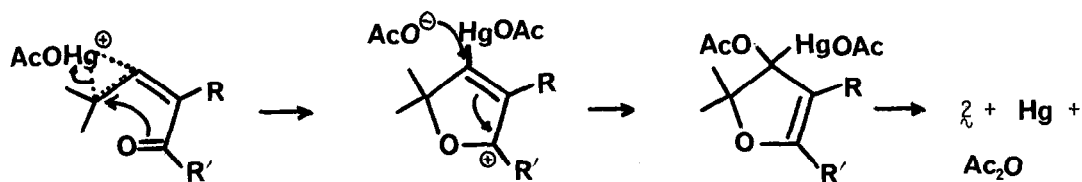
Abstract: Treatment of allenic ketones 1 with mercuric acetate yields 3(2H)-furanones 2 (90%). The oxidation of $1c$ constitutes a new synthesis of bullatenone ($2c$).

Allenic ketones such as 1 are readily available through Swern oxidation¹ of the related alcohols² and by various other routes.³ We have now found that on reaction with mercuric acetate these ketones undergo oxidative cyclization to the corresponding 3(2H)-furanones 2 .

We have reported that treatment of $1a$ with osmium tetroxide gives cyclic hemiketals that can be dehydrated to $2a$.² When applied to $1b$, however, this procedure failed. In assessing alternative oxidants we considered mercuric acetate attractive in view of its earlier use in the related conversion of vinylallenes to cyclopentenones.⁴ In the event we found that addition of $1b$ ⁵ to a suspension of mercuric acetate in glacial acetic acid at room temperature led to immediate precipitation of mercury; simple extractive work up yielded 93% of $2b$.⁶ Similar treatment of readily available $1c$ ⁷ furnished the frequently prepared,⁸ naturally occurring furanone, bullatenone ($2c$),⁹ in 91% yield.¹⁰ These conditions caused no apparent reaction with $1a$,² but the addition of a small amount of perchloric acid to the reaction mixture and then heating at 70 °C for 15 min gave 99% of $2a$.²



In light of these observations and earlier studies⁴ a reasonable mechanism for this transformation is that shown below. Addition of the metal to the more electron-rich double bond, cyclization, and attack of acetate ion can lead to acetic anhydride, mercury, and 2 .



These results provide a simple conversion of readily accessible allenic ketones to 3(2H)-furanones, a class of compounds whose synthesis has commanded considerable recent attention.^{8,11,12}

References

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- (6) This new compound has IR, ¹H NMR, and high resolution mass spectra in full agreement with its assigned structure.
- (7) We prepared $\frac{1}{2}$ (86%) by reaction of 3-methyl-1,2-butadien-1-yl lithium with N,N-dimethyl benzamide, following a known procedure: Clinet, J. C.; Linstrumelle, G. *Nouv. J. Chim.* 1977, 1, 373. Properties were in agreement with those reported for $\frac{1}{2}$: Reuter, S. M.; Salomon, R. G. *Tetrahedron Lett.* 1978, 3199.
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- (10) Our $\frac{1}{2}$ had spectroscopic properties compatible with those reported (ref. 8,9) and mp 67-68 °C (lit.⁹ mp 67.5-68.5 °C).
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- (12) We thank the National Science Foundation for support for this research.

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