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THE REACTION OF PTAD WITH (+) - PULEGONE AND MESITYL OXIDE

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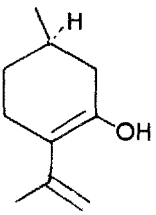
In the course of an investigation of the photoenolization of β-methyl enones[1] we have attempted to trap the photoenol[2] 1 of (+)-Pulegone(2) with a variety of dienophiles. One of the dienophiles chosen was 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD). PTAD and other triazolinediones have been investigated extensively for their reaction with dienes and other functional groups[3].

During our investigation it was observed that PTAD underwent a "dark" reaction with (+)-Pulegone. The reaction of equimolar quantities of PTAD and (+)-Pulegone in ethyl acetate at ambient temperature for 20 hours gave, on workup, a 62% yield of a mixture of the two epimeric adducts 3A and 3B. Separation (chromatography on Camag DSF-5 Silica gel) gave 3A (m.p. 184-6°) and 3B (m.p. 153-5°).



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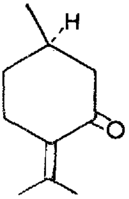

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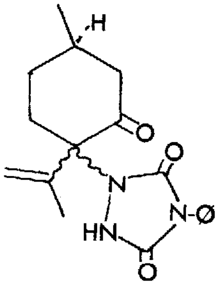
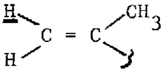
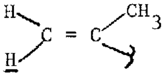
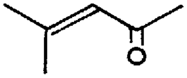


3A, 3B

Under the same conditions mesityl oxide 4 gave the adduct 5 (m.p. 120-1°) in 79% yield. The structure of 5 follows from mass spectrometry (M^+ 273, m/e 230 [M^+ - HNCO or $CH_3C{\equiv}O^+$], m/e 187 [m/e 230 - HNCO or $CH_3C{\equiv}O^+$], base peak m/e 43); infrared spectroscopy ($\nu_{max}^{CH_2Cl_2}$: 3350, 1785, 1720, 1610 cm^{-1}) and n.m.r. spectroscopy (δ^{CDCl_3}: 1.88, 3H, bs, $\underline{CH_3}$-C; 2.27, 3H, s, $\underline{CH_3}$-C=O; 5.00, 1H, s,  $(\underline{H})(H)C=C(CH_3)$; 5.20, 1H, m,  $(H)(\underline{H})C=C(CH_3)$; 5.35, 1H, s, C_3-H; 7.35, 5H, s, aromatics).



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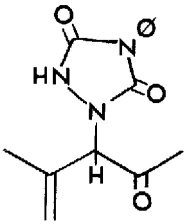

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The structures of the epimeric adducts 3A and 3B also follow from their spectral data. The mass spectra were identical for both compounds except for relative peak heights (M^+ 327, m/e 151 [M^+ - PTADH], base peak m/e 81). The infrared spectra had identical functional group frequencies ($\nu_{max}^{CH_2Cl_2}$; 3350, 1780, 1720 and 1610 cm^{-1}) and their n.m.r. spectra were different only in the peaks due to the isopropenyl group (δ^{CDCl_3}: 3A; 1.80, 3H, s, $\underline{\mathrm{CH}_3}\text{-C}<$; 4.97, 1H, s, $\begin{matrix}\underline{\mathrm{H}}\\ \mathrm{H}\end{matrix}>\mathrm{C}=\mathrm{C}<\begin{matrix}\mathrm{CH}_3\\ \end{matrix}$; 5.23, 1H, m, $\begin{matrix}\mathrm{H}\\ \underline{\mathrm{H}}\end{matrix}>\mathrm{C}=\mathrm{C}<\begin{matrix}\mathrm{CH}_3\\ \end{matrix}$: 3B; 1.85, 3H, s, $\underline{\mathrm{CH}_3}\text{-C}<$; 5.03, 1H, s, $\begin{matrix}\underline{\mathrm{H}}\\ \mathrm{H}\end{matrix}>\mathrm{C}=\mathrm{C}<\begin{matrix}\mathrm{CH}_3\\ \end{matrix}$; 5.32, 1H, m, $\begin{matrix}\mathrm{H}\\ \underline{\mathrm{H}}\end{matrix}>\mathrm{C}=\mathrm{C}<\begin{matrix}\mathrm{CH}_3\\ \end{matrix}$).

The structural changes which occur during the reaction fit the "ene-reaction" classification[4]. Mechanistically, however, the reaction may not be an "ene-reaction". Thus this reaction appears to be general only for α,β-enones which have, or can assume, an s-cis conformation. Thus 3,5,5-trimethylcyclohex-2-en-1-one (Isophorone) is recovered unchanged after several days with PTAD in ethyl acetate at ambient temperature. The reaction also seems to require a highly reactive enophile like PTAD since (+)-Pulegone does not react with Diethyl azodicarboxylate under the same conditions.

Work is presently continuing in order to establish the scope, limitations and mechanism of the reaction.[5]

References and Notes

1. J. D. Shiloff and N. R. Hunter. Unpublished work.
2. For a recent paper on the photoenolization of β-substituted enones are; M. Tada and K. Miura, Bull. Chem. Soc. Japan, 49, 713 (1976).
3. These investigations have been summarized recently; M. E. Burrage, R. C. Cookson, S. S. Gupta, and I. D. R. Stevens, J. C. S. Perkin II, 1325 (1975).
4. H. M. R. Hoffmann, Angew. Chem. Internat. Edit., 8, 556 (1968).
5. The financial assistance of the National Research Council of Canada and the Research Board of the University of Manitoba is gratefully acknowledged.