

THERMAL REARRANGEMENT OF DIENOLESTERS. SEQUENTIAL [1.3]
 SIGMATROPIC REARRANGEMENT AND INTRAMOLECULAR DIELS-ALDER CYCLO-
 ADDITION OF 1-METHYLENE-2-METHYL-2-PROPENYL HEX-5-ENOATE

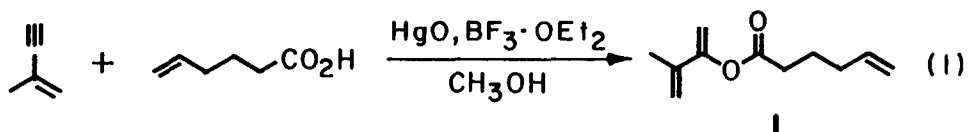
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Summary: The high temperature thermal rearrangement of the title dienol ester is reported. Its reactions entail a [1.3] acyl shift followed by intramolecular Diels-Alder cycloaddition of the resulting β -diketone.

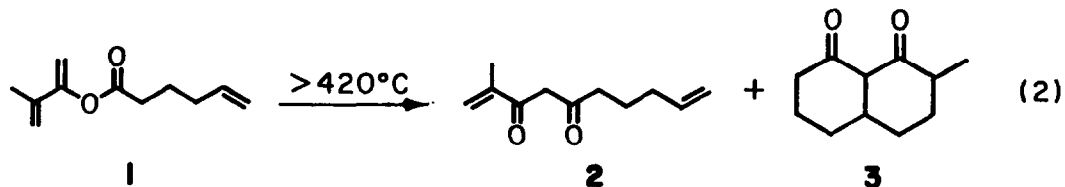
In connection with our recent studies of thermal behavior of trienes, we had occasion to examine the gas phase thermolysis of dienol ester **1**. It was our expectation that this compound would give rise to a bicyclic bridgehead enol lactone by intramolecular Diels-Alder cycloaddition.¹ We were surprised to learn that the thermal behavior of **1** was quite different from our expectations. Rather than the anticipated cycloaddition we have uncovered a novel acyl shift resulting in β -diketone formation in addition to a new variation of the intramolecular Diels-Alder reaction involving an enolic diene component. Our preliminary results from this study are reported in this communication.

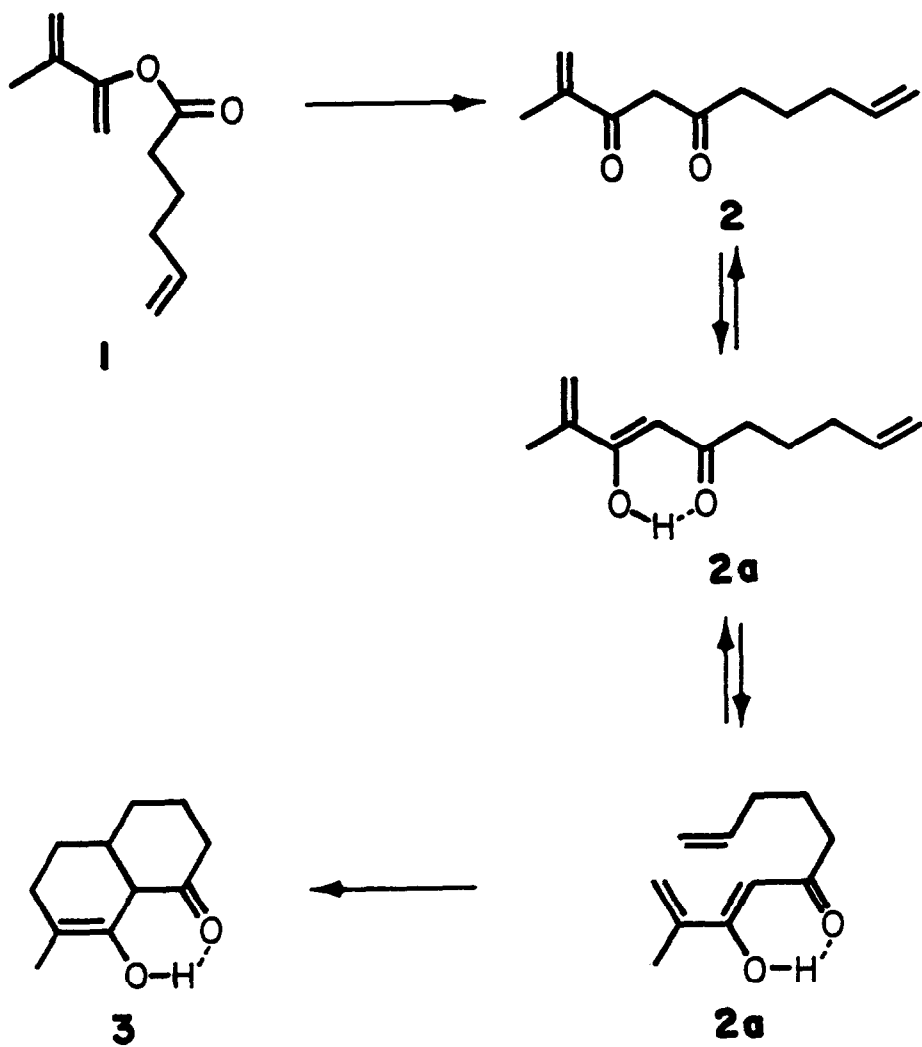
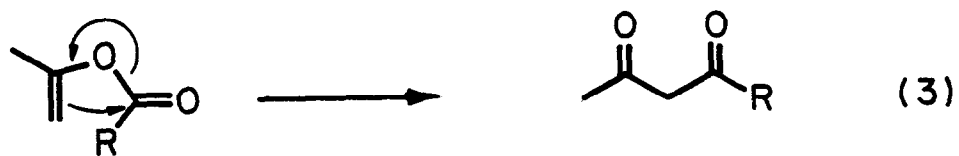
The synthesis of dienol ester **1** was accomplished by the Hg(II) catalyzed² condensation of 5-hexenoic acid with 2-methyl-1-butyne (eq 1). The reaction presumably involves electrophilic



addition of the mercuric ester to the acetylenic group.³ *In situ* protolysis of the vinyl mercury bond produces dienolester **1** and regeneration of a Hg(II) species which can reenter the reaction sequence (HgO is present in catalytic amounts). Dienol ester **1** was obtained in 35% yield.

The thermal behavior of **1** was surveyed in a gas phase flow pyrolysis apparatus. The experiment consists of passing the vapors of the substrate down a hollow quartz tube at atmospheric pressure under a stream of dry, oxygen-free nitrogen. Pyrolysis products are collected in a -78°





trap, diluted with dry pentane, and analyzed by VPC. In addition to starting material, two new products were observed (eq 2). The ratio of the three components varied as a function of both contact time (flow rate) and temperature. For example, at 400° C (12 sec) only starting material 1 and β -diketone 2 are present in a ratio of 85:15; at 433° C (12 sec) the ratio of 1:2:3 is 38:48:14. Longer contact times and higher temperatures increase the ratio of 3:2. This behavior indicates 3 is a secondary reaction product formed from the primary pyrolysis product 2. In a separate experiment 2 was subjected to the pyrolysis conditions where it was converted to 3.

Pyrolysis products were isolated by preparative VPC and characterized by their spectroscopic properties.⁴ Further support for the structure of 3 was secured by its independent synthesis from alkylation (CH_3I) of the dianion⁵ of 2,8-decalindione.⁶

A sequence of events that accounts for product formation is shown in the scheme. The first step involves formation of a new carbon-carbon bond via a formal 1,3-sigmatropic rearrangement of an enol ester (eq 3). Rearrangement of dienol ester 1 produces β -diketone 2. The onset of this reaction occurs at approximately 360° (12 sec). Efforts to induce the rearrangement in condensed media at lower temperatures (toluene, 66 h, 200° C) resulted in complex reaction mixtures. This unexpected rearrangement is in fact a precedented thermal reaction⁷ that is quite general for enol esters. For example, gas phase flow pyrolysis of isopropenyl acetate (450° C, 12 sec) results in a mixture of starting material and acetyl acetone (32:64, in > 90% mass balance). Crossover experiments indicate the isomerization is unimolecular, although the importance of surface effects has not as yet been established. We are continuing with our mechanistic investigations of this reaction.

The secondary reaction product arises from an intramolecular Diels-Alder cycloaddition. β -Diketone 2 exists predominantly in the enol form, presumably in the Z-conformation 2a. Under flow pyrolysis conditions the proton tautomerism is well catalyzed. Cycloaddition of the enolic β -diketone gives rise to a β,γ -ketoenol which upon proton tautomerism gives rise to the experimental observed isomeric mixture of methyldecalindiones 3. Although examples of Diels-Alder reactions of enols are known,⁸ we believe this is the first example of a dienol component in an intramolecular reaction. Construction of decalin ring systems utilizing both inter- and intramolecular variations of this reaction are being explored.

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References and Footnotes

1. K. J. Shea and S. Wise, *J. Am. Chem. Soc.*, 100, 6289 (1978); K. J. Shea, P. S. Beauchamp, and R. S. Lind, *J. Am. Chem. Soc.*, 102, 4544 (1980); K. J. Shea and E. Wada, submitted for publication.
2. G. F. Hennion and J. A. Nieuland, *J. Am. Chem. Soc.*, 56, 4518 (1934); C. B. Plaisance, P. F. Casalo, and G. Lavesque, *Makromol. Chem.*, 180, 79 (1979).
3. M. F. Shoslakovskii, B. A. Trofimov, A. S. Atavin, and V. I. Lavrov, *Russ. Chem. Rev.*, 37, 907 (1968).

4. Mass balance for the pyrolysis experiments varied from 55-70%. Compound 1, IR (film) 1762, 1643, 1605, 1220, 1138, 890, 870 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.80 (m, 1H), 5.2-4.8 (m, 6H), 2.48 (t, 2H, $J = 8.1$ Hz), 2.15 ('q', $J = 5.9$ Hz, 2H), 1.93 (s, 3H), 1.83 (m, 2H); ^{13}C NMR (CDCl_3) δ 171.5, 153.6, 137.6, 137.0, 115.6, 113.6, 103.2, 33.4, 33.1, 24.1, 19.4; mass spectrum, m/e (isobutane CI, relative intensity) 181 (mH^+ , 13.8), 115 (11.2), 97 (100), 85 (16.0).
- Compound 2, IR (film) 3085, 1702, 1640, 1585, 1132, 915, 800, 745 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 15.43 (s, 1H) 6.0 (s, 1H), 5.96-5.69 (m, 1H), 5.76 (br s, 1H), 5.48 (br s, 1H), 5.1-4.9 (m, 2H), 2.41 (t, 2H, $J = 7$ Hz), 2.10 (m, 2H), 1.90 (s, 3H), 1.75 (m, 2H). Minor absorptions are also observed at 5.80, 3.84, 2.56, 1.81 due to a small amount (ca. 10%) of the keto form. ^{13}C NMR (C_6D_6) δ 199.1, 181.0, 140.1, 138.2, 121.6, 115.3, 96.8, 39.3, 33.4, 24.8, 17.9; mass spectrum, m/e (isobutane CI, relative intensity) 181 (mH^+ , 100), 97 (6.0).
- Compound 3, (mixture of 2 isomers), IR (film) 2940, 2860, 1600 br, 985, 960, 850, 810 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 16.5, 16.15, (s,s, 1H), 2.6-2.2 (m, 4H), 2.2-1.5 (m, 6H), 1.5-1.0 (m, 2H), 1.22 (d, $J = 7.5$ Hz), 1.20 (d, $J = 6.8$ Hz, 3H); ^{13}C (C_6D_6) δ 194.3, 193.8, 190.1, 189.4, 100.0, 99.1, 38.7, 36.6, 36.2, 35.7, 33.2, 32.9, 31.4, 31.1, 31.0 (2c), 28.9, 27.1, 21.8, 21.7, 18.9, 17.6; mass spectrum, m/e (isobutane CI, relative intensity) 181 (mH^+ , 100), 180 (12.7), 97.
5. C. F. Hauser and T. M. Harris, J. Am. Chem. Soc., 80, 6360 (1956).
6. I. A. Kaye and R. S. Matthews, J. Org. Chem., 29, 1341 (1964).
7. F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, J. Am. Chem. Soc., 72, 3635 (1950).
8. E. Berner, Acta Chem. Scand., 10, 268 (1956); P. G. Sammes, Tetrahedron, 32, 405 (1976); P. G. Sammes and T. W. Wallace, J. Chem. Soc. Perkin Trans. 1, 1974, 415; M. Petrzilka and J. I. Grayson, Synthesis, 1981, 753.

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