

PYROLYSIS OF 2-ALLYLOXYTROPONES: A NEW ELIMINATION
REACTION TO TERMINAL DIENES

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By pyrolysis over 140°C, several 2-alkenyloxytropone gave terminal dienes and re-generated tropolones. The elimination proceeded in the electrocyclic $6\pi+2\sigma+2\sigma$ -mode on the Claisen intermediates. This was applied to a synthesis of thujosadiene.

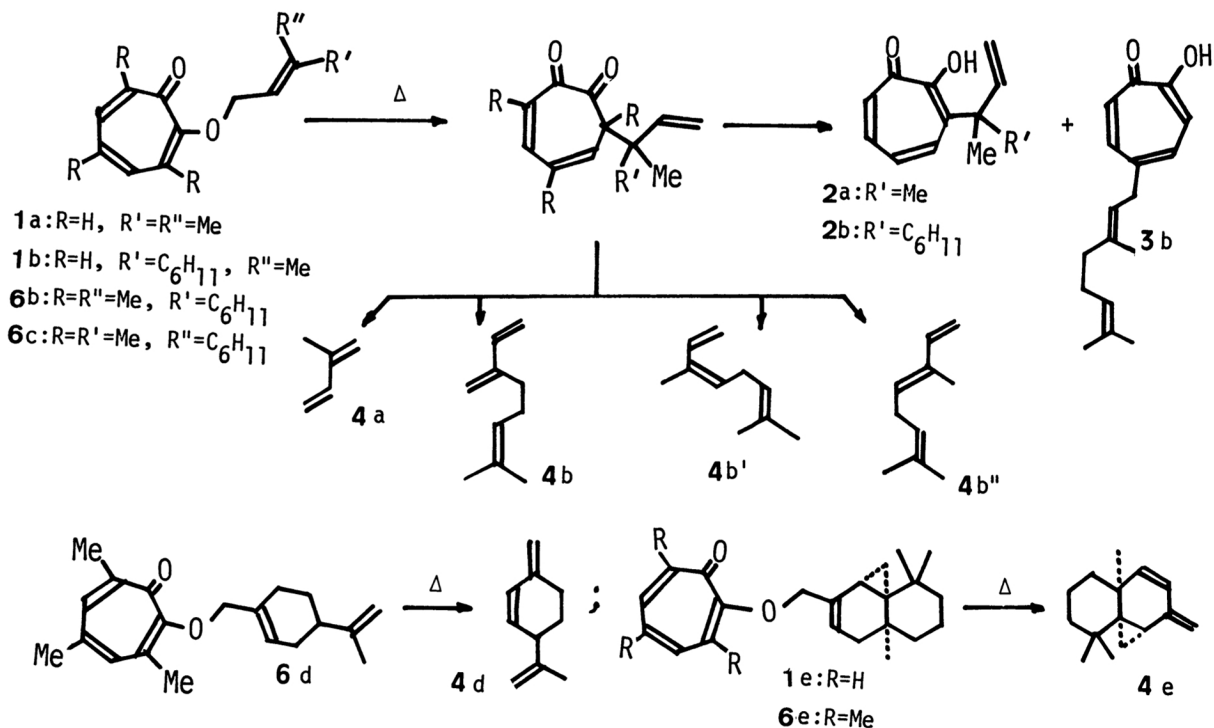
Recently, we have reported a new dimethyl sulfoxide (DMSO)-mediated radical oxidation of 2-alkoxytropone to the corresponding carbonyl compounds with a high-yield regeneration of tropolones,¹⁾ but this was not applicable to 2-(alkenyloxy)tropone which are known to cause the Claisen rearrangement, a 3,3-sigmatropy. We have now found that the 2-(2-alkenyloxy)tropone²⁾ having a γ -hydrogen atom give the terminal dienes, the elimination products derived from the intermediary Claisen products. This paper will describe the findings.

When a dioxane solution of 2-(3-methyl-2-butenyloxy)tropone (1a, 2-(prenyloxy)tropone)¹⁾ or 2-(*E*-3,7-dimethyl-2,6-octadienyloxy)tropone (1b, 2-(geranyloxy)tropone) was heated at 140°C for 2 h, the expected rearrangement products, 3-(1,1-dimethyl-2-propenyl)tropolone (2a), 50%, from the former, or 3-(1,5-dimethyl-1-vinyl-4-hexenyl)tropolone (2b), 31%, and 5-(3,7-dimethyl-2,6-octadienyl)tropolone (3b), 32%, from the latter, were obtained. As the by-products, isoprene (4a), 10%, from 1a, and myrcene (4b), 3%, *Z*-ocimene (4b'), <1%, and *E*-ocimene (4b''), 2%, from 1b, were produced together with regenerated tropolone (5a). Yields³⁾ of 4b, 4b' and 4b'' were improved to 15%, 6%, and 19% when thermolyzed at 180°C for 15 min.

Obviously, the elimination is predicted to be facilitated by an introduction of substituents on the sites of Claisen rearrangement; treatment of 2-(geranyloxy)-3,5,7-trimethyltropone (6b) at 140°C indeed afforded 4b (23%), 4b' (12%), 4b'' (36%), and the regenerated 3,5,7-trimethyltropolone (5b).³⁾ Its pyrolysis under more drastic conditions (180°C) gave 4b (30%), 4b' (8%), and 4b'' (49%); no intermediary Claisen product was detectable. Similarly, when 3,5,7-trimethyl-2-(neryloxy)tropone (6c) was heated at 140°C, the same pyrolysates as those of 6b, 4b (29%), 4b' (9%), and 4b'' (27%), were identified. The predominant formation of 4b'' over 4b' from both 6b and 6c could be attributable to the steric effect on the rearranged Claisen intermediates.

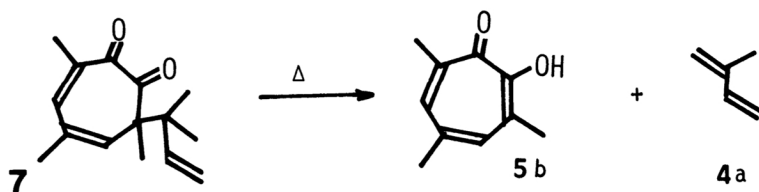
Furthermore, the ether prepared from perilla alcohol and 5b (6d, 3,5,7-trimethyl-2-(perillyloxy)tropone) was heated in DMSO at 180°C, the sole product was a

p-menthatriene, 4-isopropenyl-1-methylene-2-cyclohexene (4d, 91%), along with the regenerated 5b. Similarly, the ethers (1e and 6e) prepared from thujopsenol with 5a and 5b gave the diene (4e), 45% and 41% respectively, by heating. The 4e was identical with natural thujopsadiene.^{4,5)}

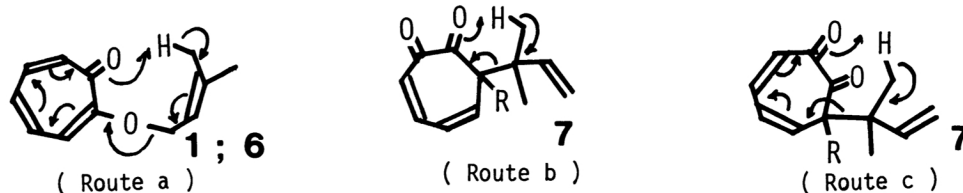


Consequently, these results, i) the same product distributions in the reaction with 6b and 6c, and ii) the facile formation of the transoid dienes, indicated an involvement of Claisen rearrangement prior to elimination.

This was further confirmed by heating at 180°C of the Claisen rearrangement product (7) prepared from 3,5,7-trimethyl-2-prenyloxypone (6a)⁶⁾ to give 5b, 95%, and 4a, a quantitative yield according to gas-liquid chromatographic analysis.

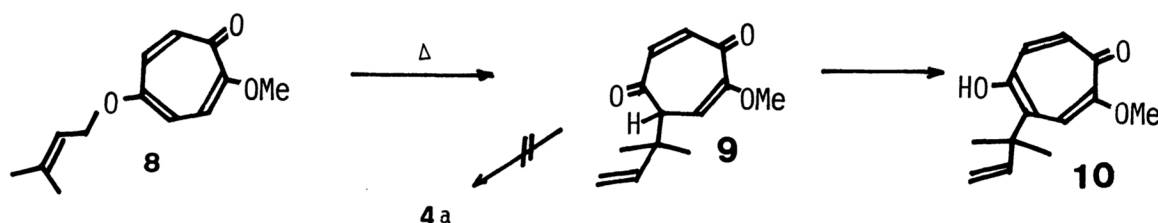


Therefore, among the possible pathways of the elimination, an $8\pi+2\sigma+2\pi+2\sigma$ -process (route a) seems to be improbable.

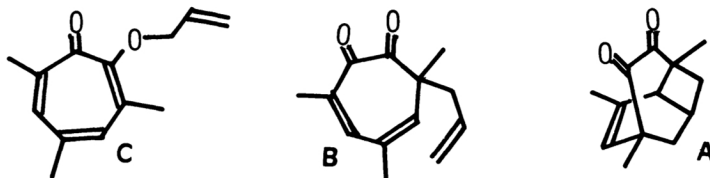


For the elimination, still there are two equally possible electrocyclic paths remained; one (route b) is the $2\pi+2\sigma+2\sigma$ -mode from the Claisen intermediate (7) and the other (route c) is the $6\pi+2\sigma+2\sigma$ -mode.

The latter seems to be favorable in the stereoelectronic point of view; the elimination has to take place *via* 7 which is in the conformation with an axial C-3 group, and such conformation fits indeed for a 3,7-sigmatropy (route c) rather than the 3,3-sigmatropy (route b) in view of non-bonding interactions. This can be checked by use of a 2- or 5-(allyloxy)tropone derivative; thus, the similar reaction of 2-methoxy-5-prenyloxy)tropone (8), whose Claisen intermediate (9) is structurally disallowed for the route b, at 160°C in DMSO gave the single product, 5-hydroxy-2-methoxy-4-(1,1-dimethyl-2-propenyl)tropone (10), 85%, and none of deallylation product could be detected.⁷⁾ Previously, we have already described a deallylation from the C-2-alkenyloxy group of 2,5-di(2-alkenyloxy)-tropone under the Claisen rearrangement conditions.⁸⁾



Previously, it was emphasized that the extreme care should be taken to prevent a hydrolysis of (allyloxy)tropone in the Claisen rearrangement, and low yields have been recorded; *e.g.*, the formation of nootkatin from 4-isopropyl-2-(prenyloxy)tropone,⁹⁾ were explained in terms of hydrolytic decomposition. However, (allyloxy)tropone are not exceptionally sensitive toward moisture, and the reported low yields should be interpreted as the result of eliminative formation of dienes from the intermediary sigmatropic products.



In connection with this, a reported formation of intramolecular Diels-Alder product (A) upon the heating of 2-allyl-3,5,7-trimethylcyclohepta-4,6-diene-1,2-dione (B), the *o*-Claisen product of 2-(allyloxy)-3,5,7-trimethyltropone (C),¹⁰⁾ must be attributable to a lack of γ -hydrogen required for the elimination.

Consequently, the facts that, i) although the yields of isolated dienes are somewhat low, estimated yields from the chromatograms are fairly well, ii) bulky allyl alcohols are more easily etherated with 5b than with 2,4,6-trimethylphenol (d),⁸⁾ and iii) the characteristic UV-absorptions of the troponeoids can be a good labelling derivative in the liquid chromatographic monitoring, should provide a simple and practical method of preparation or protection of terminal dienes in the synthetic works.

The NMR Data of the New Compounds (in CDCl_3 , δ -units from internal Me_4Si)

1b: 1.58(3H, s), 1.65(3H, s), 1.73(3H, s), 2.06(4H, s), 4.67(2H, d, $J=6$ Hz), 5.02(1H, s), 5.46

- (1H, t, J=6 Hz), and 6.6-7.2(5H, m).
- 2b: 1.47(3H, s), 1.5-2.4(4H, m), 1.51(3H, s), 1.60(3H, s), 4.97(1H, dd, J=17.5, 1 Hz), 5.06(1H, dd, J=11.5, 1 Hz), 6.26(1H, dd, J=17.5, 11.5 Hz), 6.96(1H, ddd, J=10, 7, 4.5 Hz), 7.22(2H, m), and 7.61(1H, d, J=10 Hz).
- 3b: 1.59(3H, s), 1.67(6H, s), 2.06(4H, s), 3.30(2H, d, J=7 Hz), 5.04(1H, m), 5.21(1H, t, J=7 Hz), and 7.21(4H, s).
- 6b: 1.58(3H, s), 1.67(6H, s), 2.01(4H, s), 2.31(9H, s), 4.63(2H, d, J=7 Hz), 5.02(1H, m), 5.43(1H, t, J=7 Hz), 6.76(1H, s), and 7.16(1H, s).
- 6c: 1.57(3H, s), 1.65(3H, s), 1.74(3H, s), 1.95-2.1(4H, m), 2.31(9H, s), 4.58(2H, d, J=7 Hz), 5.03(1H, m), 5.48(1H, t, J=7 Hz), 6.76(1H, s), and 7.16(1H, s).
- 5b: 1.2-2.5(6H, m), 1.72(3H, s), 2.30(9H, s), 4.42(2H, s), 4.66(2H, s), 5.75(1H, m), 6.75(1H, s), and 7.14(1H, s).
- 4d: 1.70(3H, s), 2.31(4H, m), 2.81(1H, m), 4.6-4.8(4H, m), 5.67(1H, dd, J=10, 3 Hz), and 6.17(1H, dd, J=10, 2 Hz).
- 1e: 0.60(3H, s), 0.6-2.8(11H, m), 1.09(3H, s), 1.14(3H, s), 4.78(2H, s), 5.42(1H, dm, J=6 Hz), and 6.6-7.2(5H, m).
- 8: 1.74(3H, d, J=1.5 Hz), 1.81(3H, d, J=1.5 Hz), 3.87(3H, s), 4.44(2H, d, J=7 Hz), 5.42(1H, t, sept, J=7, 1.5 Hz), 6.36(1H, ddd, J=11, 2, 1 Hz), 6.72(1H, d, J=11 Hz), 7.06(1H, dd, J=13, 2 Hz), and 7.20(1H, dd, J=13, 1 Hz).
- 10: 1.43(6H, s), 3.75(3H, s), 4.95(1H, dd, J=11, 1 Hz), 4.97(1H, dd, J=18, 1 Hz), 6.16(1H, dd, J=18, 11 Hz), 6.84(1H, d, J=14 Hz), 7.02(1H, d, J=14 Hz), and 7.25(1H, s).

References

- 1) H. Takeshita, H. Mametsuka, and N. Matsuo, *Bull. Chem. Soc. Jpn.*, 55, 1139 (1982). See also Abstract Papers of 14th Symposium of the Chemistry of Non-Benzenoid Aromatic Compounds, p 50 (Okayama, Oct. 1981).
- 2) General preparation of these ethers will be described elsewhere.
- 3) The yields recorded in this paper were those of actually isolated, except for those of isoprene which were estimated from the gas-liquid chromatograms.
- 4) S. Itô, H. Takeshita, and T. Muroi, *Tetrahedron Lett.*, 1969, 3091.
- 5) O. Motl and S. K. Pakniker, *Coll. Czech. Chem. Commun.*, 33, 1939 (1968).
- 6) R. M. Harrison and J. D. Hobson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1958.
- 7) In order to check the thermal behaviors of the benzenoid allyl ethers, we have attempted the ether-formation of D and geraniol which resulted in a formation of C-allylation product, 2-geranyl-2,4,6-trimethylcyclohexa-3,5-diene-1-one. This must be another merit of using troponyl ethers.
- 8) H. Takeshita, K. Tajiri, and I. Kouno, *Heterocycles*, 6, 1101 (1977).
- 9) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Jpn.*, 31, 782 (1958).
- 10) R. M. Harrison, J. D. Hobson, and M. M. Al Holly, *J. Chem. Soc. (C)*, 1971, 3084.

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