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# THERMAL REARRANGEMENT OF 2-(2-FURYLMETHOXY)TROPONES

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Abstract——Furfuryl ethers of tropolone and 4- and 5-isopropyltropolones afforded 3-(2-methyl-3-furyl)-, 3-(2-furylmethyl)-, 5-(2-furylmethyl)-, and 5-(5-methyl-2-furyl)tropolone derivatives. Although most of the thermolysates were structurally indistinguishable to the 3,3- or 5,5-sigmatropic products, the deuterium-labelling experiment proved all the pyrolysates to be intermolecular reaction products.

Recently, we have reported the thermal reaction of 2-(arylmethoxy)tropones to give 3- and 5-(arylmethyl)tropolones *via* radical intermediates.[1] In this connection, it will be worthwhile to investigate the thermal reaction with some hetarylmethoxytropones. We wish to describe herein the findings on the reaction with 2-(furfuryloxy)tropones which are structurally eligible for the 3,3- and 5,5-sigmatropies.

When 2-(2-furylmethoxy)tropone ( 1, colorless plates, mp 88-89.5 °C )[2] was heated in *o*-dichlorobenzene at 180 °C for 30 min, a clean reaction occurred according to NMR spectrometry. Separation of the pyrolysates was only possible by an extensive high-pressure liquid chromatography, but their methyl ethers were easily separable by a silica-gel column chromatography.

Among four rearrangement products ( 2–5 ), the least polar product, 2 ( 3% ), possessing a newly introduced substituent at C-3, was identified as two methyl ethers ( 6 and 7 ). An exhibition of the methyl singlets and the *AB*-pairs of protons on the furan rings in the NMR[3] of 6 and 7 clarified a substitution pattern of the furan moiety. Therefore, 2 must be 3-(2-methyl-3-furyl)tropolone.

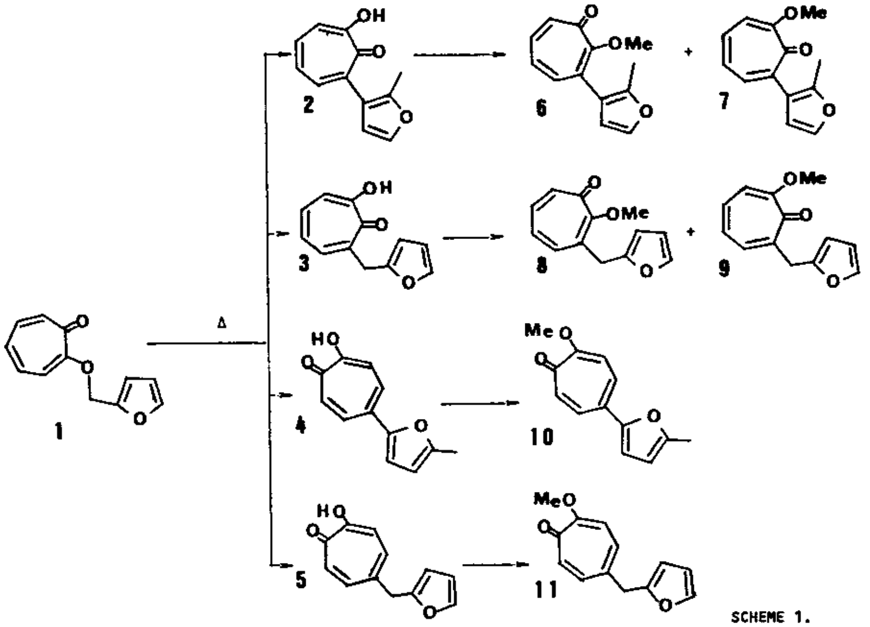
Second product, 3 ( 5% ), also characterized as two methyl ethers ( 8 and 9 ), which showed furfuryl methylene singlets and three adjacent protons on the furan ring, and deduced to be 3-(2-furylmethyl)tropolone.

The major product, 4 ( 31% ), characterized as the methyl ether ( 10, colorless needles, mp 107-109 °C ),[4] showed a methyl signal which spin-coupled with one of the two *vic*-protons on the furan ring. Thus, 4 is 5-(5-methyl-2-furyl)tropolone.

The remaining product, 5 ( 19% ), also characterized as the methyl ether ( 11 ), was 5-(2-furylmethyl)tropolone on the similar NMR analysis.

In addition to these, tropolone ( 12 ) was obtained.

Attempted regeneration of thermolysates from the methyl ethers resulted in an extensive decomposition due to an instability of the furyl moiety under the hydrolytic conditions. Nevertheless, the $^{13}$C-NMR spectra of the troponoid carbons of these methyl ethers were almost superimposable to those of 3- and 5-(arylmethyl)-tropolone methyl ethers,[1] with which, an umbigious evidence for their strctures was obtained.



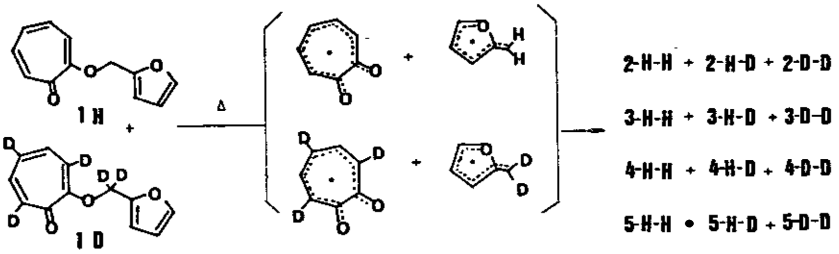
SCHEME 1.

Concomittant formation of **2** and **3** can not be explained in terms of a concerted reaction;[5] at least in part, a non-concerted process might play a role. To check this, we have carried out the deuterium labelling experiments. The pentadeuterated **1**, **1**-$d_5$ ( **1D** ), was prepared by the Vowinckel's phenyl ether preparation[6] with 3,5,7-tropolone-$d_3$ ( with an isotopic purity, $P_i$>95%, **12**-$d_3$ ) and (2-furyl)methan-$d_2$-ol ( $P_i$>95% ), prepared from methyl 2-furoate and $LiAlD_4$. After the thermolysis of a 1:1-mixture of **1D**[6] and **1**-$d_0$ ( **1H** ) under the same conditions, the products were isolated and their deuterium contents were analyzed by the mass spectrometry. As compiled in Table 1, an extensive shufling of two moieties throughout the products, **2** to **5**, has occurred. Therefore, they must be the stepwise intermolecular products as depicted in scheme 2.

Preferential occurrence of a non-concerted rearrangement over a concerted sigmatropy, *e,g.*, 3,3- or 5,5-process,[8] is similar to thermolysis of 2-(arylmethoxy)tropones. In addition, when a 1:1-mixture of **1** and 2-methoxytropone ( **13** ) was heated at 180 °C, thermolysates identified were only **2**–**5** and the recovered **13** ( 100% ).

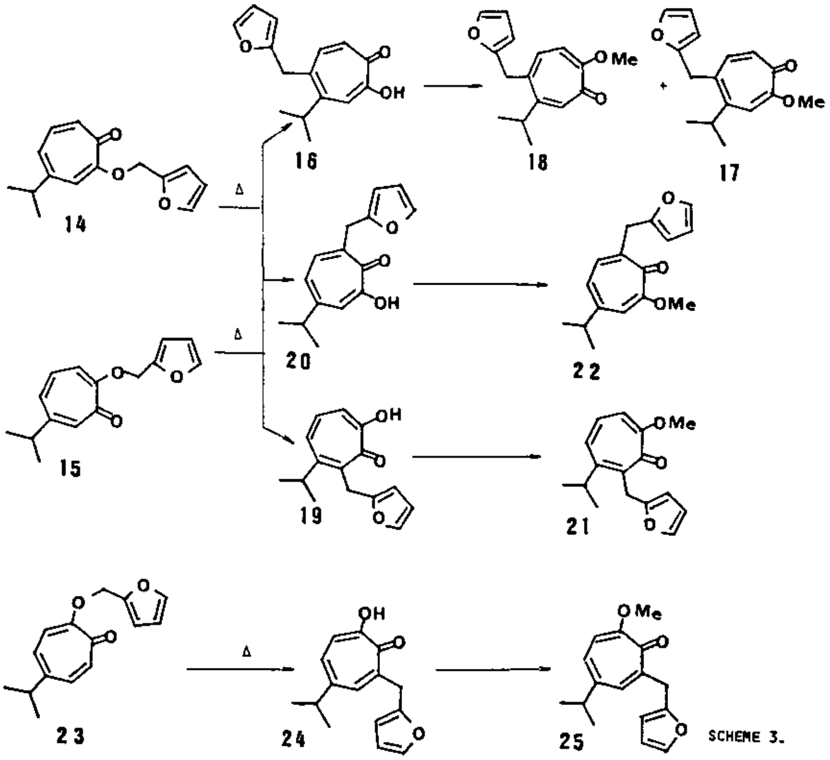
TABLE 1. DEUTERIUM DISTRIBUTIONS OF THE THERMOLYSATES FROM THE 1:1-MIXTURE OF 1-$d_5$ AND -$d_0$.

| | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ |
|---|---|---|---|---|---|
| 2 | 25.2 | 5.0 | 26.0 | 11.0 | 32.8 |
| 3 | 25.0 | 4.8 | 25.8 | 12.4 | 32.0 |
| 4 | 26.5 | 10.0 | 13.9 | 17.2 | 32.4 |
| 5 | 27.6 | 6.0 | 22.0 | 13.2 | 31.2 |



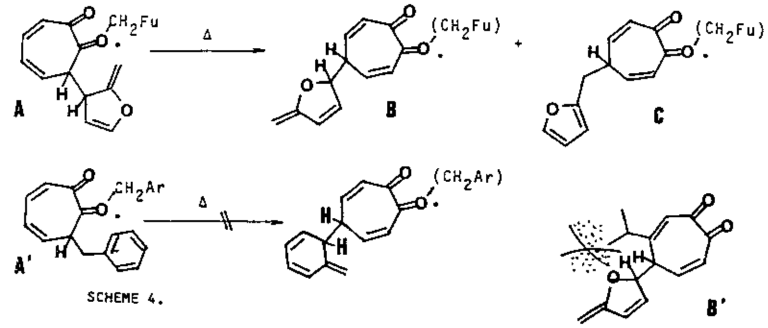
SCHEME 2.

The absence of 6–11 suggests that 13 is not a radical chain-carrier. Then, should the reaction be proceeded *via* above mentioned cleavage-recombination process, two 2-furylmethyl ethers from hinokitiol may reveal identical product distributions. Indeed, 2-(2-furylmethoxy)-4- ( 14 ) and 2-(2-furylmethoxy)-6-isopropyltropones ( 15 )[9] were separately subjected to the thermolysis; the major product formed in each case was 5-(2-furylmethyl)-4-isopropyltropolone ( 16 ) isolated after chromatography in the form of methyl ethers ( 17 and 18 ). Along this, a formation of two minor thermolysates ( 19 and 20 ) was also indifferent; they were again characterized as methyl ethers ( 21 and 22 ) and shown to be 3- and 7-(2-furylmethy)-4-isopropyltropolone.



SCHEME 3.

Furthermore, the thermolysis of γ-thujaplicin derivative ( 23 ) showed a formation of single product, 3-(2-furlymethyl)-5-isopropyltropolone ( 24 ) which was easily purified as a methyl ether, 2-(2-furylmethyl)-5-isopropyl-7-methoxytropone ( 25 ). Now, we like to point out the product distribution differences between 2-(2-furylmethoxy)- and 2-(arylmethoxy)tropones:[1] With latters, the C-3 rearrangement products were predominant over C-5, but the major thermolysates from 1 were 5-substituted tropolones. This is only explainable in terms of facilitation of a secondary process in the latters; *i.e.*, a primarily formed A is capable of further 3,3-sigmatropy to B and C, while the equivalent species ( A' ) from arylmethyl radicals are only capable of the rearrangement by an expense of the resonance energy for the 6π-system. This also fits to the predominance of 16 from 14 and 15; the other 3,3-product ( B' ) from a protoproduct might suffer a large steric hindrance due to the isopropyl group.



SCHEME 4.

In conclusion, 2-(2-furylmethoxy)tropones upon thermolysis have intermolecularly afforded the 3- and 5-rearrangement products in high yields. A care should be therefore taken not to deduce the mechanism of the thermolysis on structural ground only.

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REFERENCES

1. H. Takeshita, H. Mametsuka, A. Chisaka, and N. Matsuo, *Chem. Lett.*, **1981**, 71.
2. The elemental analyses of pyrolysates were performed as methyl ethers, for which the pertinent figrures have been obtained.
3. Throughout the study, the NMR spectra were measured in CDCl$_3$ solutions. All the compounds described herein gave pertinent figures: *e.g.*, **6**: 2.25(3H, s), 3.73(3H, s), 6.40(1H, d, J=2 Hz), 6.6-7.0 (4H, m), and 7.31(1H, d, J=2 Hz). **7**: 2.28(3H, s), 3.92(3H, s), 6.54(1H, d, J=2 Hz), 6.6-7.0(4H, m), and 7.29(1H, d, J=2 Hz). **8**: 3.89(3H, s), 4.01(2H, s), 6.03(1H, dd, J=3, 1 Hz), 6.27(1H, dd, J=3, 2 Hz), 6.7-7.1(4H, m), and 7.28(1H, dd, J=2, 1 Hz). **9**: 3.92(3H, s), 4.09 (2H, s), 6.14(1H, dd, J=3, 2 Hz), 6.28(1H, dd, J=3, 2 Hz), 6.6-7.0(3H, m), 7.20(1H, m), and 7.29 (1H, dd, J=2, 1 Hz). **10**: 2.37(3H, d, J=1 Hz), 3.95(3H, s), 6.08(1H, dq, J=3, 1 Hz), 6.57(1H, d, J=3 Hz), 6.79 (1H, d, J=10.5 Hz), 7.24(1H, d, J=13 Hz), 7.44(1H, dd J=10.5, 1.5 Hz), and 7.56 (1H, dd, J=13, 1.5 Hz). **11**: 3.91(3H, s), 3.86(2H, s), 6.06(1H, dd, J=3, 1 Hz), 6.31(1H, dd, J=3, 2 Hz), 6.68 (1H, d, J=10 Hz), 6.94(1H, dt, J=10, 1 Hz), 7.16(2H, d, J=1 Hz), and 7.32(1H, dd, J=2, 1 Hz). The $^1$H-NMR spectra of the other thermolysates will be included in a full paper.
4. Other than this **10**, every pyrolysate behaved as a colorless oil.
5. R. B. Woodward and R. Hoffmann, "The Conservation of the Orbital Symmetry", Verlag Chemie, GmbH, Weinheim, 1970, p 114.
6. E. Vowinkel, *Chem. Ber.*, 99, 1479 ( 1966 ).
7) Labelled deuterium on the tropone ring was partly exchanged during the etherification. Mass-spectral determination, which was performed with a JEOL OS1G spectrometer, of **1**-*d* showed $d_1:d_2:d_3:d_4:d_5$=0.0:1.1:2.0:13.2:30.6:53.1.
8. For the 5,5-sigmatropy, see G. Frater and H. Schmid, *Helv. Chim. Acta*, 51, 190 ( 1968 ).
9. In general, two isomeric ethers derived from hinokitiol are difficult to separate; the mixture of **14** and **15** was only separable by means of intensive high-pressure liquid chromatography ( μ-Polasil/ ethyl acetate-hexane ).

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