Tetrahedron Letters No. 35, pp 3049 - 3052, 1977. Pergamon Press. Printed in Great Britain.

CYCLOADDITION REACTION OF STYRYLTROPONES WITH MALEIC ANHYDRIDE

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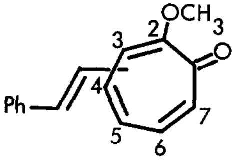
(Received in Japan 1 June 1977; received in UK for publication 8 July 1977)

In the previous paper (1), we have described the highly regioselective cycloaddition reactions with the inverse electron demands occurring between the N=N-C=C heterodiene system in arylazotropones and cyclopentadiene. Further reactions with cyclopropene (2) disclosed the endo stereochemistry required for this type of reactions, although the regioselectivity was somewhat reduced. We have extended the reaction to styryltropones in order to investigate the regioselectivity in homodiene system in the similar environment and subsequently found that the reaction involving side chain have also occurred in one case, but only with the electron-deficient dienophile.

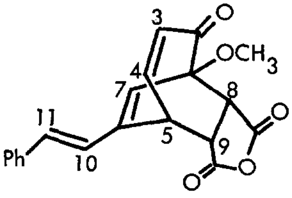
Although unreactive with cyclopentadiene under various conditions, 2-methoxy-4-styryltropone 1 (3), and 2-methoxy-6-styryltropone 2 (3) underwent cycloaddition reaction within a few hours with maleic anhydride in refluxing xylene. A single product from 1 and two from 2 were detected by TLC, and isolated by SiO_2 chromatography. The product 3 obtained in 26% yield from 1 has the spectral properties shown in Table from which structure was deduced (4). PMO calculation (5) revealed that 3 was derived from one of the most stabilized transition states.

One of the products 4 obtained from 2 in 48% yield was hydrolysed and then converted to the dimethyl ester, spectral analysis of which (Table) (4) disclosed the endo. stereochemistry required by the reaction.

The second product 5 (7% yield) from 2 is also an 1 : 1 adduct (M^+ 336) having no anhydride linkage but a carboxyl and a lactone groupings (ν 3100, 1735, 1710-1690, 1620, 1600 cm^{-1}). For the spectral analysis, 5 was converted to the methyl ester 6. PMR and PMDR spectra of 6 clearly exhibits the presence of the aliphatic carbon sequence $-C_{(5)}H_2-C_{(4)}HPh-C_{(3)}H-CO_2Me$ [δ_3 3.99 (br.d, J=5.0), δ_4 3.12 (br.ddd,



1: 4-styryl
2: 6-styryl
10: 5-styryl



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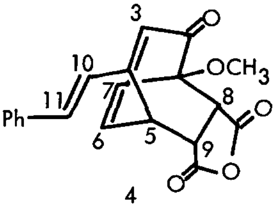

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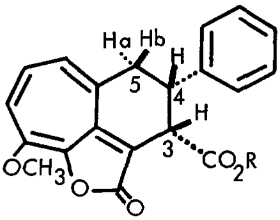
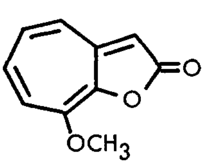
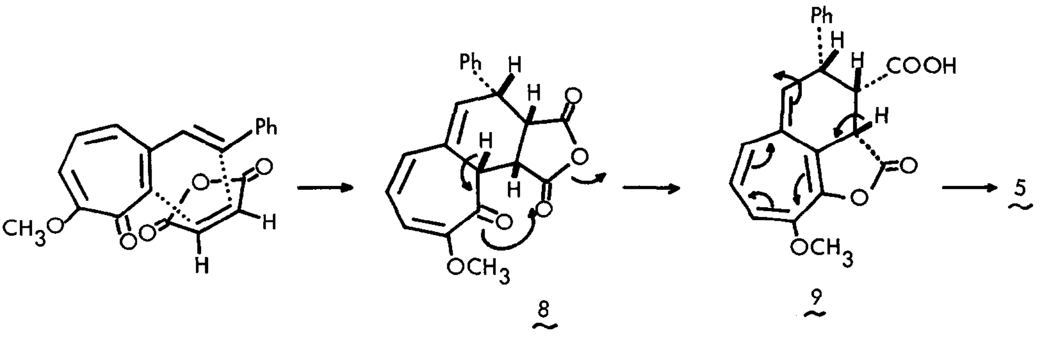


5: R=H
6: R= Me



7

J=13.0, 5.0, 3.0), δ_{5a} 3.90 (br.dd, J=16.0, 13.0), δ_{5b} 2.96 (br.dd, J=16.0, 3.0), δ_{Me} 3.38 (3H, s), δ_{Ph}~7.3 (5H, complex)] in addition to that of a methoxyl group [δ_{Me} 4.11 (3H, s)] (6) and three vinylic hydrogens [δ~6.9 (3H, complex)] on a tropone ring. Furthermore, its UV spectrum [λmax 229 (log ε 4.26), 257 (sh, 4.04), 273 (sh, 4.24), 282 (4.30), 291 (4.27), 380 (4.00), 399 nm (4.11)] is almost superimposable with that of 7 recently obtained by Takase, et al. (7). The formation of 5 is understood as shown below by the cycloaddition (to 8) followed by the lactonization (to 9) and subsequent rearrangement (to 5 via thermally allowed [1,9]-sigmatropy or acid catalized hydrogen shift). Thus, another example of cycloaddition involving the side chain double bond was found in tropone series, and the endo orientation in the reaction was deduced from coupling constant in 6 ($J_{3,4}$=5 Hz).



Both 4 and 5 are formed through transition states with the largest stabilization energy (5).

2-Methoxy-5-styryltropone 10 (8) failed to react with maleic anhydride under the conditions described above, but underwent reactions with cyclopentadiene in xylene (150°, 22 hrs), and with tetracyanoethylene in benzene (40°, 2 days) to give complicated mixtures.

Although the difference in the behavior of 1, 2 and 10 toward cycloaddition reaction is not fully understood, it may reflect the conformational difference.

Table. Physical Properties of the Products (10)

3 : yellow prisms, m.p. 96-97°, MS m/e 336 (M^+), 308, 280, 264, 210 (b.p.); UV λmax 221 (log ε 4.12), 229 (4.10), 237 (4.06), 280 (4.21), 290 (4.22), 298 (4.19), 310 (sh, 4.19), 360 (3.16), 396 nm (sh, 2.78); IR ν 1862, 1780, 1672, 750, 690 cm^{-1}; PMR (acetone-d_6) δ_{Me} 3.69 (3H, s), δ_3 5.92 (br.d, J=11.0), δ_4,δ_{Ph} ~7.4 (6H, m), δ_5 4.49 (br.d, J=9.0), δ_7 6.04 (br.s), δ_8 4.27 (d, J=9.0), δ_9 4.19 (dd, J=9.0, 2.0), δ_{10},δ_{11} 6.96 (2H, br.s).

dimethyl ester correspond to 4 : colorless oil; IR ν 1740, 1655, 1610, 1585 cm^{-1}; PMR δ_3 5.69 (br.s), δ_5 4.37 (br.d, J=7.5), δ_6 6.71 (br.dd, J=9.5, 7.5), δ_7 6.37 (br.d, J=9.5), δ_8 3.71 (br.d, J=11.0), δ_9 3.24 (br.d, J=11.0), δ_{10} 6.73 (br.d, J=16.5), δ_{11} 7.15 (d, J=16.5), δ_{Ph} ~7.4 (5H, complex), δ_{Me} 3.55, 3.64, 3.68 (each 3H, s).

5 : reddish orange prisms; m.p. 256° (dec.); MS m/e 336 (M^+), 293, 292 (b.p.), 263; UV λmax 229 (log ε 4.24), 283 (4.31), 290 (4.25), 384 (4.00), 402 nm (4.10).

6 : reddish orange prisms; m.p. 159-159.5°; MS m/e 350 (M^+), 292, 291 (b.p.), 263; IR ($CHCl_3$) ν 1750 (sh), 1730 (sh), 1725 (s) cm^{-1}.

References and Notes

1) S. Itô and I. Saito, *Tetrahedron Letters*, 1203 (1977).

2) Y. Fujise, M. Sakaino and S. Itô, *ibid.*, in press (1977).

3) H. Matsumura, *Nippon Kagaku Zasshi*, **77**, 300 (1956).

4) For PMR spectra of the similar systems, see S. Itô, H. Takeshita and Y. Shoji, *Tetrahedron Letters*, 1815 (1969).

5) K. Fukui in "Molecular Orbitals in Chemistry, Physics and Biology", P.O. Lowdin and B. Pullman, ed. Academic Press, N.Y. (1964). HMO was used for both cycloaddend and the interactions between HOMO and LUMO are only considered.

6) a) H. Sugiyama, Ph.D. Thesis, Tohoku University, 1963. b) S. Itô, K. Takase, N. Kawabe and H.

Sugiyama, Bull. Chem. Soc. Japan, **39**, 253 (1966).

7) Compound **7** has the following absorption maxima: λmax 224 (log ε 4.20), 263 (4.18), 281 (4.27), 289 (sh, 4.23), 371 (4.09), 389 nm (4.18). [K. Takase, M. Yasunami, A. Chen and A. Minoya (1975) to be published.] We thank Professor Takase and Dr. Yasunami for their information prior to publication.

8) Obtained by CH_2N_2 methylation of 5-styryltropolone (9): pale yellow plates, m.p. 131.5-132°.

9) H. Matsumura, Nippon Kagaky Zasshi, **81**, 1763 (1960), H. Higashi, K. Kurosawa and H. Matsumura, Bull. Chem. Soc. Japan, **43**, 3236 (1970).

10) The spectra was measured under the following conditions: MS at 70 eV, UV in methanol, IR in KBr for crystals and $CHCl_3$ for liquid, PMR in $CDCl_3$, unless otherwise stated.