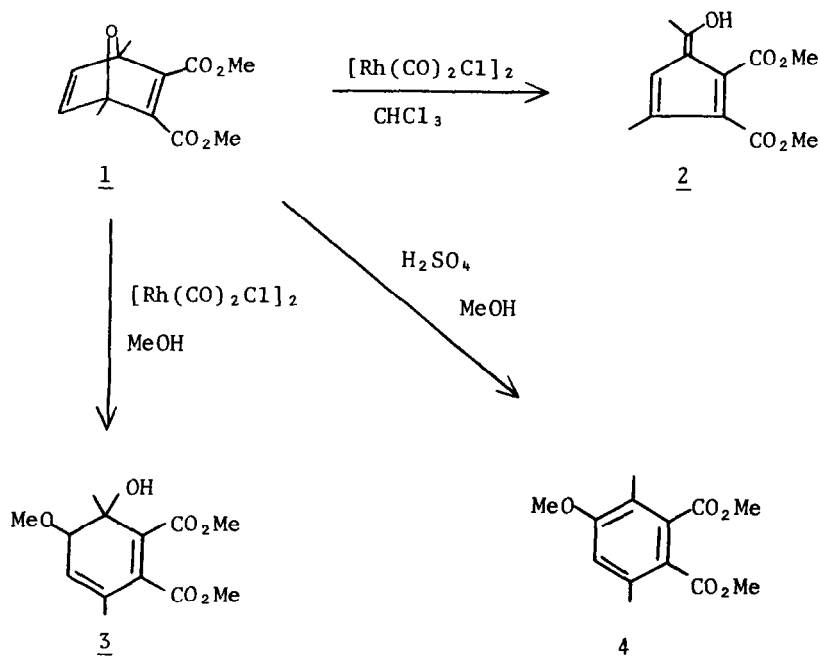


STEREOCHEMISTRY OF THE $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ -CATALYZED REACTION OF
7-OXABICYCLO[2.2.1]HEPTA-2,5-DIENES WITH METHANOL

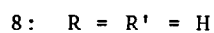
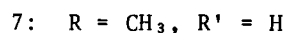
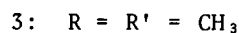
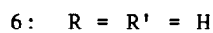
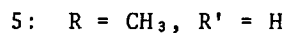
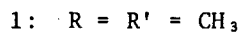
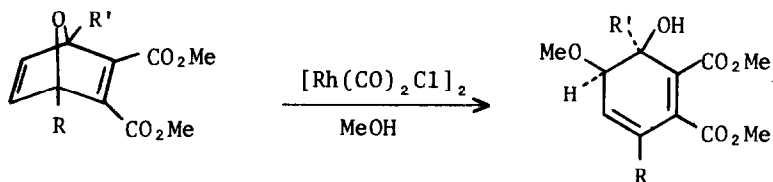
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Previous studies by Hogeveen and coworkers have established that 1,4-dimethyl-2,3-dicarbomethoxy-7-oxabicyclo[2.2.1]hepta-2,5-diene (1) undergoes rearrangement to 3,6-dimethyl-1,2-dicarbomethoxy-6-hydroxyfulvene (2) on treatment with catalytic amounts of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in chloroform.^{1,2,3} In methanol the rhodium catalyst effects addition of methanol to 1 to afford methoxycyclohexadienol 3⁴; the stereochemistry of 3 was not established. Acid-catalyzed reaction of some highly substituted oxabicycloheptadienes with methanol also affords methoxycyclohexadienol derivatives⁵, but the sole product isolated from the acid-catalyzed reaction of 1 with methanol is the aromatic derivative 4⁴.

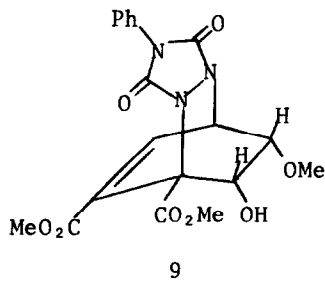


In order to determine the stereochemistry of the reaction in methanol, the conversion of 1 to 3 was repeated; and the reaction was extended to the conversion of 5⁶ and 6⁷ to 7 and 8, respectively. All reactions were carried out as described previously for 1⁴ except the reactions were allowed to proceed for 3 hr at 0-5° C.⁸ Diene 3 was crystallized from hexane as a crystalline solid, m.p. 90-91° C. According to NMR, 5 and 6 were quantitatively converted to dienes



7⁹ and 8¹⁰, respectively. Attempted purification by distillation or chromatography resulted in aromatization. Treatment of 7 and 8 with CF₃CO₂H effected quantitative aromatization to dimethyl 3-hydroxy-6-methylphthalate and dimethyl 3-hydroxyphthalate, respectively.

Since it is not possible to determine the stereochemistry of the hydroxy and methoxy groups from the nmr spectrum of 7 and 8 due to uncertainty of the conformation of the carbocyclic ring, the diene 8 was converted to Diels-Alder adduct 9 by reaction with N-phenyl-1,2,4-triazoline-3,5-dione.¹² The large coupling constant observed for the hydrogens on the same carbons as the hydroxy and methoxy groups (8.0 Hz) is consistent only with cis stereochemistry in the adduct and, consequently, in 8.¹³ The stereochemistry in 3 and 7 is assigned cis by analogy with 8.



9

The cis dihydroxy derivative 10 corresponding to 8 (MeO- replaced by HO-) was also prepared from 6 as an oil in quantitative yield by using 1:1 H₂O/THF in place of methanol in the [Rh(CO)₂Cl]₂-catalyzed reaction.¹⁷ Treatment of 10 with CF₃CO₂H effected quantitative aromatization to a mixture of dimethyl 3- and 4-

hydroxyphthalate.

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REFERENCES

1. A. Bruggink and H. Hogeveen, Tetrahedron Letters, 4961 (1972).
2. H. Hogeveen and T. B. Middelkoop, Tetrahedron Letters, 4325 (1973).
3. R. Roulet, J. Wenger, M. Hardy and P. Vogel, Tetrahedron Letters, 1479 (1974).
4. H. Hogeveen and T. B. Middelkoop, Tetrahedron Letters, 3671 (1973).
5. K. Reiff, U. Schumacher, G. Stubenrauch and W. Tochtermann, Tetrahedron Letters, 1553 (1973).
6. K. Alder and K. H. Backendorf, Justus Leibigs Ann. Chem., 535, 101 (1938).
7. O. Diels and K. Alder, Justus Leibigs Ann. Chem., 490, 243 (1931).
8. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was purchased from Pressure Chemical Co., Pittsburgh, PA 15201.
9. Spectral data for 7: ir (CHCl_3), 3570, 1720, 1650, 1580 cm^{-1} ; nmr (CDCl_3) δ 1.8 (3H, m), 2.3 (1H, br s), 3.5 (3H, s), 3.83 (3H, s), 3.88 (3H, s), 4.11 (1H, m), 4.75 (1H, m), 5.95 ppm (1H, m).
10. Spectral data for 8: ir (CHCl_3), 3550, 1725, 1645, 1580 cm^{-1} ; nmr (CDCl_3) δ 3.45 (3H, s), 3.78 (3H, s), 3.81 (3H, s), 4.0 (1H, m), 4.73 (1H, d, $J = 6$ Hz), 6.25 ppm (2H, m).

11. Satisfactory analyses were obtained for the adduct; nmr (CDCl₃) δ 3.53 (3H, s), 3.66 (1H, d, 8 Hz), 3.8 (3H, s), 3.91 (3H, s), 4.45 (1H, d, 8 Hz), 5.25 (1H, m), 7.43 ppm (5H, s).
12. R. C. Cookson, S. S. Gupta, I. D. R. Stevens and C. T. Watts, Org. Synth., 51, 121 (1971).
13. See ref. 14-16 for similar examples of establishment of stereochemistry of substituted 1,3-cyclohexadienes from the nmr spectra of Diels-Alder adducts of the dienes with maleic anhydride. The N-phenyl 1,2,4-triazoline-3,5-dione adduct of t-butyl trans-2-methoxy-3-acetoxy-2,3-dihydrobenzoate shows the expected coupling of 3.1 Hz for the trans hydrogens on the same carbons as the methoxy and acetoxy groups.
14. D. T. Gibson, M. Hensley, H. Yoshioka and T. J. Mabry, Biochemistry, 9, 1626 (1970).
15. D. T. Gibson, B. Gschwendt, W. K. Yeh and V. M. Kobal, Biochemistry, 12, 1520 (1973).
16. R. M. DeMarinis, C. N. Filer, S. M. Waraszkievicz and G. A. Berchtold, J. Amer. Chem. Soc., 96, 1193 (1974).
17. Spectral data for 10: ir (CDCl₃) 3400 (br), 1725, 1640 (w) cm⁻¹; nmr (CDCl₃) δ 3.18 (2H, br s), 3.86 (6H, br s), 4.26 (1H, d, J = 7 Hz), 4.66 (1H, d, J = 7 Hz), 6.23 ppm (2H, br s).