A New Synthesis of the Tricyclic [10]Annulene 7b-Methyl-7bH-cyclopent-[cd]indene

Zev Lidert and Charles W. Rees

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

In a new versatile synthesis of the tricyclic [10]annulene, 7b-methyl-7bH-cyclopent[cd]indene, the third ring is formed by an intramolecular aldol condensation rather than a cycloaddition reaction.

We have recently reported the synthesis of the tricyclic [10]annulene (1),¹ and certain of its peripherally substituted derivatives, based on the [8 + 2] cycloaddition reactions of 3-methoxy-3a-methyl-3aH-indene (2).² We now report an alternative synthesis of (1) which avoids this cycloaddition of the labile 3aH-indene (2), provides a route to differently substituted derivatives of (1), and circumvents the very rapid aromatising rearrangement which 3aH-indenes undergo when the ring junction substituent is other than a simple alkyl group.³

Birch reduction and methylation of 7-methoxyindan-1-one (3),⁴ in the standard way,² gave the methoxydienone (4),[†] b.p.



84—87 °C at 0.1 mmHg, which was converted by phenylselenation and oxidation into the methoxytrienone (5),† m.p 79—81 °C, in 30% overall yield from (3). Acid hydrolysis of the dienone (4) gave the expected diketone (6) (75%), m.p. 75—76 °C, a useful synthetic intermediate.

The methoxytrienone (5) was converted into the tricyclic ketone (10) in 50% overall yield, as follows. Treatment of (5) with lithium methyl vinyl ether in tetrahydrofuran (THF) at $-78 \,^{\circ}\text{C}^5$ gave the alcohol (7) which was deprotonated with dimsyl-sodium in dimethyl sulphoxide and methylated with methyl iodide⁶ to give (8). Acid hydrolysis of (8), without purification, gave the diketone (9) which was then cyclised with 5% aqueous methanolic potassium hydroxide, followed

[†] Spectral data for selected intermediates: (4) v_{max} (film) 1743 cm⁻¹; δ (CDCl₃) 1.33 (3H, s, 7a-Me), 2.2—2.9 (6H, m, 2-, 3-, and 5-CH₂), 3.62 (3H, s, MeO), 4.68 (1H, br.t, J 4 Hz, 6-CH), 5.70—5.75 (1 H, m, 4-CH). (5) v_{max} (film) 1705 cm⁻¹; δ (CDCl₃) 1.39 (3H, s, 7a-Me), 2.89 (1H, dt, J 22 and 6 Hz) and 3.04 (1H, dt, J 22 and 2 Hz), (5-CH₂), 3.62 (3H, s, MeO), 4.65 (1H, dd, J 6 and 2 Hz, 6-CH), 6.00 (1H, d, J_{2.3} 5 Hz, 2-CH), 6.06 (1H, dd, J 6 and 2 Hz, 4-CH), 7.65 (1H, d, J_{2.3} 5 Hz, 3-CH). (10) δ (CDCl₃) 1.30 (3H, s, 7b-Me), 2.75—2.90 (4H, m, 6- and 7-CH₂), 3.55 (3H, s, MeO), 5.68—5.72 (2H, m, 1-CH and 5-CH), 5.91 (1H, d, J 6 Hz) and 6.26 (1H, d, J 6 Hz) (3- and 4-CH).



Scheme 1. Reagents: i, K, Bu^tOH, THF, LiBr, NH₃, -78 °C; ii, MeI, THF, NH₃, -78 °C; iii, LiNPr¹₂, THF, -78 °C; iv, PhSeCl, THF, -90 °C; v, H₂O₂, THF, pyridine, 0 to 5 °C; vi, 2M HCl, H₂O, THF; vii, CH₂=C(Li)OMe, THF, -78 to 0 °C; viii, 20% NH₄Cl, H₂O; ix, MeSOCH₂⁻Na⁺, 20 °C; x, MeI; xi, 5% KOH, H₂O, MeOH; xii, di-isobutylaluminium hydride, hexane; xiii, MTPI, HMPA; xiv, 10% NaOH, H₂O; xv, p-MeC₆H₄SO₃H (catalytic), CH₂Cl₂; xvi, KH, 18-crown-6, DME, -20 °C; xvii, FSO₃Me, -20 °C to reflux (DME).

J. CHEM. SOC., CHEM. COMMUN., 1982

by chromatography on silica gel, to give the pure tricyclic ketone $(10)^{\dagger}$ as a viscous oil.

Reduction of the ketone (10) with di-isobutylaluminium hydride in hexane gave a mixture of the epimeric alcohols (11), which could be separated chromatographically. However, the mixture (11) was readily dehydrated with methyltriphenoxyphosphonium iodide (MTPI) in hexamethylphosphoric triamide (HMPA) at room temperature, followed by stirring with 10% aqueous sodium hydroxide for 1 h.⁷ Immediate treatment of the tetraene (12) with a catalytic amount of 4toluenesulphonic acid in methylene dichloride at room temperature for 5 min gave the [10]annulene (1), identical with that reported earlier,¹ in 42% overall yield from (10).

The tricyclic ketone (10) is a versatile intermediate for synthesising [10]annulene derivatives. Thus, with two equivalents of potassium hydride in 1,2-dimethoxyethane (DME) containing 18-crown-6, followed by addition of methyl fluorosulphonate and subsequent heating to reflux for 30 min, it gave the 2-methoxy compound (13) as a yellow oil (70%) identical with that prepared by an alternative route.⁸

Our efforts to introduce substituents other than alkyl groups on to the central carbon of the annulene (1) will be reported later.³

A postdoctoral award from the Swedish Natural Science Research Council to Z. L. is gratefully acknowledged.

Received, 10th February 1982; Com. 140

References

- 1 T. L. Gilchrist, D. Tuddenham, R. McCague, C. J. Moody, and C. W. Rees, J. Chem. Soc., Chem. Commun., 1981, 657.
- 2 T. L. Gilchrist, C. W. Rees, and D. Tuddenham, J. Chem. Soc., Perkin Trans. 1, 1981, 3214.
- 3 H. C. Gibbard, unpublished work.
- 4 L. B. Magnusson, C. A. Craig, and C. Postumus, J. Am. Chem. Soc., 1964, 86, 3958.
- 5 J. E. Baldwin, O. W. Lever, and N. R. Tzodikov, J. Org. Chem., 1976, 41, 2874.
- 6 B. Sjöberg and K. Sjöberg, *Acta Chem. Scand., Ser. B*, 1972, 26, 275.
- 7 M. Casey, unpublished work.
- 8 R. McCague, unpublished work.