4a-Methyl-4a*H*-fluorenes

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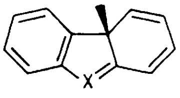
The monobenzo derivative (**1**) of 3a-methyl-3a*H*-indene and its methyl derivative (**3**) have been synthesised; although isolable they are reactive, undergoing autoxidation, dimerisation, and other [4 + 2]cycloadditions, thermal and acid catalysed aromatisation to fluorenes, and photochemical rearrangement to naphthalenes.

We have recently described the synthesis and chemistry of 3-methoxy-3a*H*-indene, the first example of an isolable bicyclic polyene in which the peripheral conjugation is interrupted by only one saturated carbon at a ring junction.[1] Such systems are of interest because of the variety of cycloaddition reactions and sigmatropic rearrangements which they very readily undergo. By extending the conjugation into an additional fused aromatic ring, we hoped to produce stable compounds which could be more fully examined. The 4a*H*-carbazole (**2**), an aza analogue of the benzo fused system, was too reactive for isolation,[2] but we now report that the benzo system itself, 4a*H*-fluorene (**1**), and its methyl derivative (**3**), can be isolated and stored for short periods in cold dilute solution, although they are still sensitive, reactive compounds.



(1) X = CH
(2) X = N
(3) X = CMe

The 4a-methylfluorene skeleton was formed by reaction of the tetrahydrofluoren-1-one (**4**),[3] available from indene and 4-chlorobutyronitrile, with lithium dimethylcuprate to give the 4a-methylhexahydrofluoren-1-one (75%).† Bromination and dehydrobromination of this gave the enone (**5**) which was further dehydrogenated with the recently described iodylbenzene–benzeneseleninic anhydride combination[4] to give 4a-methyl-4,4a-dihydrofluoren-1-one in 40% overall yield from (**4**). Many other reagents were applied to this dehydrogenation sequence without success. Reduction with di-isobutylaluminium hydride (DIBAL) gave the alcohol (**6**) which was unstable to air, chromatography, and distillation, but was substantially pure (n.m.r.) as formed and could be stored in dilute solution at 0 °C for extended periods. Dehydration of alcohol (**6**) with toluene-*p*-sulphonic acid (0.1 mol) in benzene with azeotropic removal of water, followed by flash chromatography gave 4a-methyl-4a*H*-fluorene (**1**) in 20% overall yield from ketone (**4**).

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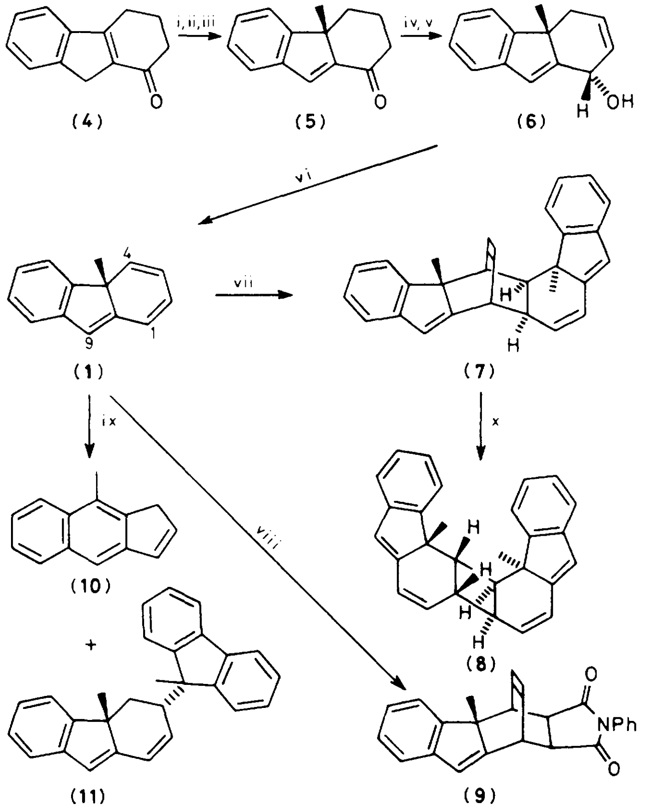
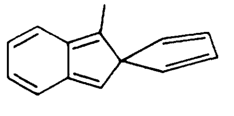
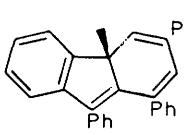
† All new compounds, which were pale yellow oils except where noted, were fully characterised spectroscopically, particularly by difference n.O.e. and by microanalysis, usually of crystalline derivatives, and/or by accurate mass measurement.



Scheme 1. i, $LiCuMe_2$, Et_2O, -20 °C, 2 h; ii, *N*-bromosuccinimide, CCl_4, reflux, 30 min; iii, 1,5-diazabicyclo[5.4.0]undec-5-ene, CCl_4, reflux, 30 min; iv, $PhIO_2$, $(PhSeO)_2O$, C_6H_6, reflux, 2 h; v, DIBAL, C_6H_6-hexane, 0 °C, 2 h; vi, toluene-*p*-sulphonic acid, C_6H_6, reflux, 25 min; vii, CCl_4, 60 °C, 18 h; viii, *N*-phenylmaleimide, CCl_4, 20 °C, 5 days; ix, $h\nu$ (254 nm), hexane, 1 h; x, toluene-*p*-sulphonic acid, $CDCl_3$, CD_3COCD_3, 20 °C, 5 days.

Hydrocarbon (**1**) is a pale yellow mobile oil which polymerises and oxidises rapidly when neat.[‡][§] On standing in neutral solution it slowly dimerises to the [4 + 2]cycloadduct (**7**), m.p. >310 °C decomp.;[‡] a 1 M solution in tetrachloromethane dimerised almost completely within 18 h at 60 °C. On treatment with protic or Lewis acids the unsymmetrical dimer (**7**) is converted into a second, symmetrical dimer (**8**), a waxy solid, m.p. 150—180 °C decomp. The structures of the dimers were assigned following spin decoupling and difference n.O.e. experiments; for (**8**) the wide shift dispersion of the aromatic resonances (δ 5.8—7.2) ruled out the three other symmetrical stereoisomeric structures. Compound (**8**) could have arisen from (**7**) by protonation of either of the original C-9 positions, cleavage of the C-1–C-3′ bond, and reclosure of the resulting highly stabilised carbonium ion to give the more stable isomer. Both (**7**) and (**8**) were characteristic by-products in most reactions of hydrocarbon (**1**), their relative concentrations depending upon the acidity of the medium.


(**12**)



(**13**)

4a-Methyl-4a*H*-fluorene (**1**) also adds dienophiles such as *N*-phenyltriazolindione and *N*-phenylmaleimide in a [4 + 2] manner. The former gave an unstable product which was characterised by rapid n.m.r. spectroscopy and the latter gave cycloadduct (**9**) as a semisolid glass. No products of [8 + 2]-cycloaddition, characteristic of 3a*H*-indenes,[1] could be detected, but it is not surprising that this mode is completely suppressed by the benzo fusion. Curiously, chlorosulphonyl isocyanate failed to give a cycloadduct, but acted instead as a powerful catalyst for the formation of (**7**) and (**8**).

Aromatisation of (**1**) is brought about by strong protic acids or by flash vacuum pyrolysis (FVP). When (**1**) is treated with an excess of hydrobromic and acetic acids in refluxing tetrachloromethane a mixture of 4- and 1-methylfluorenes (10:1) (n.m.r.) is formed in high yield; presumably the major isomer arises by a 1,2-shift of methyl to a C-4 carbonium ion, the most stable of which would result from protonation at C-9. With toluene-*p*-sulphonic acid (1 mole) in refluxing benzene, the symmetrical dimer (**8**) is also formed since aromatisation is now slower. FVP of (**1**) at 650 °C and 0.03 mmHg gave 9-methylfluorene (50%) as the major product, formed presumably by successive [1,5] sigmatropic methyl shifts. 9,9′-Bifluorenyl, m.p. 246 °C,[5] was also isolated (25%) from both the pyrolysate and the oven residues; it is possibly formed in the condensed phase, by formation and dimerisation of fluorenyl radicals, and then sublimes.

Photolysis of (**1**) in hexane gave 9-methylcyclopenta[*b*]-naphthalene (**10**) (20%) as pale yellow low-melting crystals, the dimer (**7**) (10%) (a thermal product), 9-methylfluorene (3%), and the 'dimer' (**11**) (30%), m.p. 130—160 °C decomp. The last product is derived from further reaction between 9-methylfluorene and starting material (**1**), possibly by hydrogen transfer, one of the reactants being in a photoexcited state, and collapse of the radical pair so formed. Consistent with this, in methanol or acetonitrile as solvent formation of the photodimer (**11**) was suppressed, its place being taken by an equivalent amount of 9-methylfluorene, while the yields of the other products were substantially unaltered. Presumably these solvents differ from hexane in that they can themselves deactivate the photoexcited precursor of photodimer (**11**). The cyclopentanaphthalene (**10**) is thought to arise by a di-π-methane type rearrangement, analogous to that invoked to explain the formation of cyclopentaquinolines from 4a*H*-carbazoles.[2] As in the latter reaction, none of the alternative double bond isomer was formed (n.m.r., including difference n.O.e.), and a blank experiment showed that these isomers do not interconvert under the reaction conditions. These observations argue against an alternative mechanism proceeding through the spiro compound (**12**) since this intermediate would have to show remarkable selectivity in its rearrangement to produce isomer (**10**) exclusively.

4a,9-Dimethyl-4a*H*-fluorene (**3**)[§] has also been prepared in a similar synthesis starting from 1,3-dimethylindene and 4-chlorobutyronitrile, and its physical, spectroscopic, and chemical properties all closely parallel those described for (**1**). The only 4a*H*-fluorenes previously reported were 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene (**13**), a stable yellow solid formed

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[‡] Elemental analysis showed the correct carbon to hydrogen ratio, but a specimen completely free from oxidised products could not be obtained.

[§] Selected spectroscopic data: (**1**) λ_{max} (EtOH) 394 (ϵ 2700, sh), 371 (4900), 358 (4700), 333 (3200, sh), 318 (2700, sh), 303 (2400, sh), 292 (2200, sh), and 244 nm (17 000); ν_{max} (liq. film) 2970, 2920, 1462, 870, 845, 750, 710, and 670 cm^{-1}; $\delta(^1H)(CDCl_3$; 250 MHz) 1.42 (s, Me), 5.84—6.01 (m, 2-H and 3-H), 6.46—6.54 (m, 1-H, 4-H, and 9-H), and 7.0—7.35 (m, 5—8-H); (**3**) λ_{max} (EtOH) 396 (ϵ 2300, sh), 373 (3800), 358 (3600), 335 (2200, sh), 319 (1800, sh), 303 (1700, sh), 288 (1700, sh), and 245 nm (13 500); ν_{max} (liq. film) 2960, 2920, 1470, 1387, 751, 715, and 670 cm^{-1}; $\delta(^1H)$ $(CDCl_3)$ 1.40 (s, 4a-Me), 2.11 (s, 9-Me), 5.96—6.00 (m, 2-H and 3-H), 6.46 (dt, *J* 8.5 and 1 Hz, 4-H), 6.57 (br. d, *J* 9 Hz, 1-H), and 7.07—7.35 (m, 5—8-H).

in low yield by polyphosphoric acid induced self-condensation of acetophenone, and a series of its products of electrophilic substitution in the 4-position.[6] Compound (**13**) is clearly very much stabilized by the three phenyl substituents.

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