Tetrahedron Letters,Vol.23,No.21,pp 2223-2224,1982 0040-4039/82/212223-02$03.00/0
Printed in Great Britain

A SYNTHESIS OF 2-METHYLENEINDANE

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Summary After difficulties encountered in a conventional Wittig approach, a synthesis of 2-methyleneindane was achieved via a β-silylsulphone intermediate.

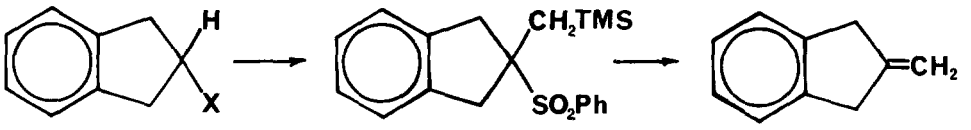
As part of a continuing study of the chemistry of ozonides, we required a preparative quantity of 2-methyleneindane (3)[1]. In this paper we describe the difficulties encountered in the conventional Wittig approach and a successful synthesis via β-silylsulphone intermediates.

The conventional Wittig reaction between indan-2-one and methylenetriphenylphosphorane was unsuccessful due to extensive enolisation of the ketone by the unstabilised ylid.[2] To overcome the enolisation problem, the sense of the Wittig reaction was reversed and the reaction between formaldehyde and 2-indanylidenetriphenylphosphorane was attempted The reaction of 2-bromoindane[3] and triphenylphosphine [1 1, sealed tube, 140°, 24h.] afforded a phosphonium salt[4] which on conversion [1 1 eq. n-BuLi, Et_2O, 0°C] into the corresponding ylid followed by treatment with formaldehyde [-20°C, 1h] gave exclusively 1-methyleneindane[5] When the above sequence was repeated using 2-chloroindane, 1-methyleneindane was again obtained as the sole product.

Although 2-bromoindane undergoes normal S_N2 reactions with stabilised carbanions[3], the above observations are consistent with triphenylphosphine reacting as a base rather than a nucleophile. An initial base-promoted dehydrohalogenation of the 2-haloindane would give indene and triphenylphosphonium halide. Subsequent protonation of indene would be expected to occur exclusively at the 2-position with concomitant generation of a stabilised carbonium centre at the 1-position which would be captured readily by triphenylphosphine or a halide ion. The overall result is clearly the formation of the 1-indanylphosphonium salts rather than the expected 2-indanylphosphonium salts. In a separate experiment it was shown that indene and triphenylphosphonium bromide [toluene, reflux under N_2, 8h] afforded a phosphonium salt which in turn produced 1-methyleneindane[5] when subjected to the Wittig reaction procedure.

2-Methyleneindane (3) was successfully prepared via a β-silylsulphone (see Scheme). Free radical addition of thiophenol to indene [1.1 1, AIBN (1.5 mol %), 60-80°C petrol, 70°, 5h] gave exclusively 2-indanyl phenyl sulphide (1a) which, without purification, was oxidised [30% H_2O_2, Ac_2O/AcOH, 15°] to the corresponding sulphone (1b, 90%)[6]. Treatment of the sulphone (1b) with n-butyl lithium [THF, under N_2, 0°C, 5 min] followed by iodomethyltrimethylsilane [1.25 eq , -5°C, 20 min, then RT, 20h] gave the required β-silylsulphone (2, 85%)[7] which was converted [$Bu_4NF.3H_2O$(3 eq), THF, reflux, 1h] into the required

2-methyleneindane (3) [(84%) overall yield from indene 64%] The analytical and spectroscopic data obtained were entirely consistent with structure (3)[8].



1 a, X=SPh
b, X=SO2Ph

2

3

Scheme

The above example demonstrates an efficient alternative method to the Wittig reaction for the production of terminal olefins, particularly where enolisation or elimination are a problem. Further extensions of this procedure are under investigation.

Acknowledgements. The author wishes to thank Mr. A. Flinn for some preliminary experiments, Dr. P.N. Preston for helpful discussions and Dr I.H. Sadler (University of Edinburgh) for ^{13}C NMR spectra.

References

1 2-Methyleneindane has been reported as a minor solvolysis product. J. Wilt, W.W. Pawlikowski and J.J. Wierczorck, J.Org.Chem , 1972,37,820.

2 G. Witchard and C.E. Griffin, J.Org.Chem., 1964,29,2335.

3. T.H.Porter and W. Shive, J.Med.Chem., 1968,11,402.

4. Crude yield, 46%, m p. (from CH_2Cl_3/EtOAc), 224-7°C

5 The ^1H and ^{13}C NMR spectral data are identical to those obtained from an authentic sample. (I.H. Sadler, private communication).

6. A.A. Oswald, J.Org.Chem., 1960,25,467.

7. m p. (from Et_2O) 113-5°C (Calculated for $C_{19}H_{24}O_2SSi$ C,66.2, H 7.08%, found C,66 1, H 7 2%), $\delta_H(CDCl_3$, TMS) 0.16 (9H,s), 1.51 (2H,s,-CH_2-), 3.05 (2H,d,J=0.7 Hz), 4.08 (2H,d,J=0.7 Hz), 7.30 (4H,s), 7.72 (3H,m), 8.10 (2H,m).

8. Colourless oil, b p. 94-96/1mm Hg (Calculated for $C_{10}H_{10}$ C,92 25, H,7.75%, found C,92.5, H, 7.8%), $\delta_H(CDCl_3$, TMS) 3.64 (4H,m,-CH_2-), 5.04 (2H,m,=CH_2), 7.10 (4H,s,arom.) $\delta_C(CDCl_3$, TMS) 39.29 (t), 107 69 (t,=C), 124 33 (d,α-arom.C), 126.31(d,β-arom.C), 142.20(s), 148.55(s).

(Received in UK 24 March 1982)