High Asymmetic Induction in a Photo-Diels–Alder Addition[1]

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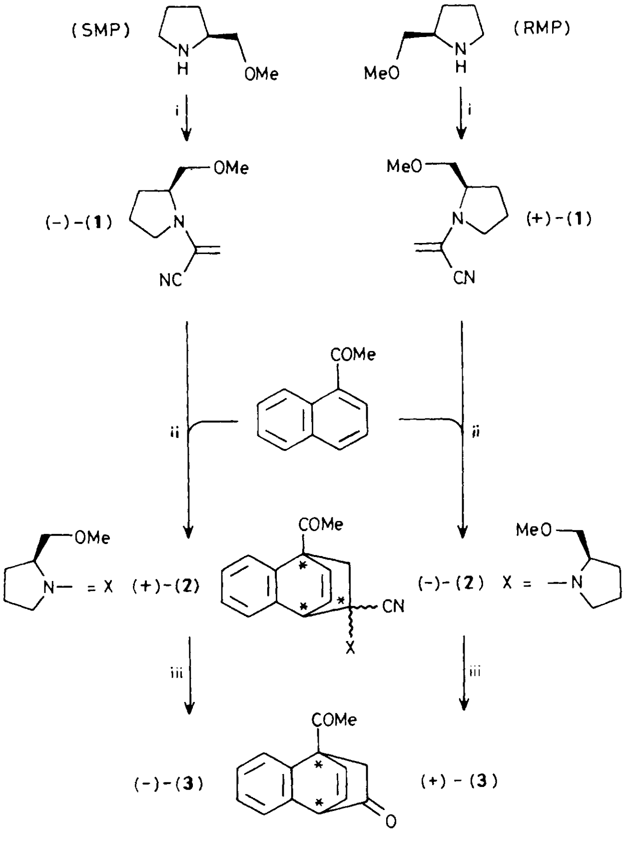
(*S*)-α-(2-Methoxymethyl-1-pyrrolidinyl)-acrylonitrile (*S*)-(**1**) and its (*R*)-enantiomer undergo efficient (2 + 4) photoaddition to electronically excited 1-acetylnaphthalene to form the adducts (+)- and (−)-(**2**); hydrolysis of the latter yields the chiral 1,4-diketones (−)- and (+)-(**3**) in ≥97% enantiomeric excess.

A highly regio- and stereo-selective light induced 1,4-addition of the C=C bond of captodative alkenes to 1- and 2-acylnaphthalenes has been reported.[2,3] We report here that extensive asymmetric induction may be achieved in this reaction.

The readily available chiral auxiliaries (*S*)-2-methoxymethylpyrrolidine (SMP)[5] and its (*R*)-enantiomer (RMP)† were converted‡ into the captodative[4] α-amino-acrylonitriles (*S*)-(**1**) {$[\alpha]_D^{20}$ −14.4°, *c* 0.7, cyclohexane} and (*R*)-(**1**), respectively, in moderate yield. (2 + 4)-Addition of these alkenes to photoexcited 1-acetylnaphthalene in cyclohexane under the conditions reported previously[2] gave the 1,4-adducts (+)-(**2**) {m.p. 115 °C, $[\alpha]_D^{20}$ +21.3°, *c* 0.2, $CHCl_3$} and (−)-(**2**) {m.p. 114—115 °C, $[\alpha]_D^{20}$ −20.3°, *c* 0.2, $CHCl_3$}, respectively, as sole products (isolated yield 62%). At 40 °C in C_6D_6, (+)-(**2**) undergoes retrocleavage to the starting materials with *k* $5 \times 10^{-5}\,s^{-1}$ and half life 3.9 h. This limited stability hampers both its recovery and further conversion.

During the photoaddition, three new stereogenic centres are formed. However, the absolute configuration at carbons 1, 4, and 9 in the adducts (**2**) has not yet been determined. It is probable, however, that the methoxymethylpyrrolidinyl moiety is in a *syn*-position relative to the benzenoid ring as



Scheme 1. i, HCl, $ClCH_2CHO$ [liberated from $ClCH_2CH(OMe)_2$], reflux; NaCN, 8—10 °C; NaOH, 8—10 °C; ii, *h*ν (≥280 nm), cyclohexane, room temp; iii, $CuSO_4/H_2O/Na_2HPO_4$, room temp.

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† Used as purchased from Merck-Schuchardt.

‡ By adaption of the procedure for preparation of α-morpholinoacrylonitrile (m.p. 62.5—63.5 °C) reported by S. C. Temin, *J. Org. Chem.*, 1957, **22**, 1714. It should be noted, however, that (*S*)- and (*R*)-(**1**), in contrast to α-morpholinoacrylonitrile, are sensitive liquids and considerable losses with formation of dark resinous decomposition products may occur upon bulb-to-bulb distillation even at 62 °C; 0.2 mmHg, and that the preparation has not yet been optimized. The samples used gave satisfactory elemental analyses and their i.r. and ^1H n.m.r. spectra were fully in accord with the structures shown. This statement also applies to both enantiomers each of (**2**) and (**3**).

previously found for the donor groups in two other (2 + 4)-adducts of captodative alkenes to 1-acetylnaphthalene.[2,3] Hydrolysis of either enantiomer of (**2**) in the presence of copper(II) sulphate and disodium hydrogenphosphate[6] destroys the centre of chirality at C(9) while liberating (−)-(**3**) {m.p. 114—116 °C, $[\alpha]_D^{20}$ −8.6°, *c* 0.1, methanol) and (+)-(**3**) {m.p. 114—116 °C, $[\alpha]_D^{20}$ +8.5°, *c* 0.1, methanol), respectively, with preparative yield of 76% and ≥97% enantiomeric excess.§ The chiral auxiliaries SMP and RMP may be recovered in good yield.

This work has been supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. Earlier stages of this investigation were supported by Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

Received, 6th August, 1987; Com. 1161

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§ H.p.l.c. of both (−)- and (+)-(**3**) with hexane–propan-2-ol (9 : 1) on isotactic poly(tritylmethacrylate) as the stationary phase kept at 0 °C revealed the presence of not more than 1% of the other enantiomer. When racemic (**3**) (m.p. 84—85 °C) was subjected to the same conditions, two totally separated peaks with equal areas and retention times of 4.55 min for (+)-(**3**), and 5.96 min for (−)-(**3**) were detected.

References

1 Taken in part from the diploma thesis (1987) and planned doctoral thesis of M. Pies, Universität Duisburg.
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