Tetrahedron Letters,Vol.27,No.43,pp 5301-5302,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

AN EFFICIENT SYNTHESIS OF 9-PHENANTHROLS

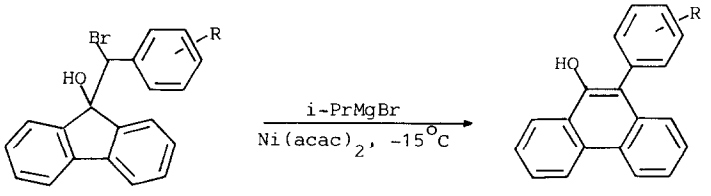
Amnard Tantivanich* and Doungrudee Supatimusro

Department of Chemistry, Kasetsart University

Pholyotin Road, Bangkok 10900, Thailand

ABSTRACT : *The nickel(II)acetylacetonate catalyzed reaction of 9-(α-bromobenzyl)-9-fluorenols with Grignard reagent affords 10-phenyl-9-phenanthrols in good yield under mild conditions*

Although many routes to synthesize the 10-substituted-9-phenanthrols are now available,[1-6] modified processes are still of interest. We wish to report an efficient access to 10-phenyl-9-phenanthrol(2)system involves the ring expansion of 9-fluorenyl derivatives(1)with Grignard reagent under catalysis by nickel(II)acetylacetonate.[7,8]



1 a-f 2 a-f

The following procedure for ring expansion of 9-(α-bromobenzyl)-9-fluorenol 1a is representative : a solution of 1a (0.35 g, 1 mmol) in 1:1 benzene-ether (8 mL) and $Ni(acac)_2$ (0.002 g, 0.009 mmol) are stirred under nitrogen at -15°C. To this is added a solution of isopropylmagnesium bromide (4 mmol) in ether (8 mL) and stirring is maintained for 2 hr. After work-up and chromatography on silica gel afforded compound 2a. Recrystallization from CCl_4 gives pure 10-phenyl-9-phenanthrol; yield 0.243 g (90%); m.p.138-140°C (Lit,[9] m.p.140-141°C). MS (70 ev) : m/e (relative intensity %) = 270 (M^+, 100); IR (KBr) : ν = 3525 cm^{-1} (OH); ^{1}HNMR ($CDCl_3$/TMS) : δ = 5.43 (s, OH, 1H), 7.10-7.87 (m, ArH, 11H), 8.23-8.88 ppm (m, ArH, 2H). The acetate derivative has a m.p. of 150-151°C (Lit,[9] m.p. 153-155°C), ^{1}HNMR ($CDCl_3$/TMS) : δ 2.05 ppm (s, CH_3COO, 3H). Results of ring-enlarged compound 2 compared to those uncatalyzed are illustrated in the Table.

Table : Ring Expansion of 9-(α-bromobenzyl)-9-fluorenols 1a-f

Product	R	Yield[a,b] [%]	m.p., [°C]	Acetate, m.p., [°C]
2a	H	90(70)	138-140	150-151
2b	*m*-F	88(68)	145-146	120-121
2c	*m*-Cl	71(67)	125-126.5	102-103
2d	*p*-Cl	74(65)	132-133	159-160
2e	*m*-$CHBr_2$	72(64)	119-120	106-107.5
2f	*p*-$CHBr_2$	75(62)	167-168	148-150

a) Isolated yield after recrystallization

b) Value in brackets is yield of uncatalyzed reactions

The facility of the procedure and the high yield of products make this method attractive for the synthesis of compound 2. Another advantage is that the method allows one to prepare the 10-phenyl-9-phenanthrols with substituents in the phenyl ring. Further studies on the use of other catalysts along with the mechanistic investigations are now underway.

Acknowledgements

We are grateful to Professor R.W. Rickards, The Australian National University, Canberra, Australia, for measurements of mass spectra, elemental analyses, and his helpful discussion. This work was partially supported from the National Research Council of Thailand.

References and Notes

1. C.F. Koelsch, J. Am. Chem. Soc., 1934, 56, 480.
2. C.K. Bradsher and W.J. Jackson, Jr., J. Am. Chem. Soc., 1954, 76, 734.
3. W. Ried and R. Conte, Chem. Ber., 1972, 105, 799.
4. S. Kobayashi, K. Kitamura, A. Miura, M. Fukuda, and M. Kihara, Chem. Pharm. Bull. 1972, 20, 694.
5. G. Koebrich and J. Grosser, Tetrahedron Lett., 1972, 13, 4117.
6. A.J. Sisti, J. Org. Chem. 1970, 35, 2670.
7. Starting 9-benzyl-9-fluorenols were prepared from 9-fluorenone (C.L. Areus and M.M. Coombs, J. Chem. Soc., 1954, 3977). Subsequence bromination with NBS gives the compound 1a-f.
8. a) D. Supatimusro, Master of Science thesis, Kasetsart University, 1986.
   b) All products exhibited physical and spectral characteristics in accordance with the assigned structures.
9. R.C. Fuson and S.J. Strycker, J. Am. Chem. Soc., 1957, 79, 2633.

(Received in UK 26 August 1986)