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An Unusual Route to 1,4-Diphenyl-2,3-Dimethylbutadiene-1,3*

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SUMMARY

Treatment of 2,3-dimethyl-2,3-diphenylbutanediol-1,4-ditosylate with tetra-n-butylammonium bromide in dimethylacetamide did not give the expected 2,3-dimethyl-2,3-diphenyl-1,4-dibromobutane but,rather, by a double phenonium ion rearrangement, 1,4-diphenyl-2,3-dimethylbutadiene-1,3. 2,3-Dimethyl-2,3-diphenyl-1,4-dibromobutane was required as starting material for the synthesis of head to head poly(α-methylstyrene) by Grignard coupling.

INTRODUCTION

In our continued effort to synthesize head to head (H-H) polymers (MALANGA,VOGL 1983) we were interested in preparing H-H poly(α-methylstyrene) (MALANGA et al.1983). For our approach,we needed to synthesize 2,3-dimethyl-2,3-diphenyl-1,4-dibromobutane which was to be transformed into the mono-Grignard reagent and treated with a copper complex to polymerize it to H-H poly(α-methylstyrene). This sequence of reactions had been successfully applied previously for the synthesis of H-H polyisobutylene (MALANGA 1982).

RESULTS AND DISCUSSION

A rearrangement reaction was observed when 2,3-dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (I) was treated with tetraalkylammonium bromide in dimethylacetamide (DMAc) at 110°C. The only isolated product was 1,4-diphenyl-2,3-dimethylbutadiene-1,3 (II).

Nucleophilic displacement reaction of the tosylate by the bromide ion has been used by us to prepare 2,2,3,3-tetramethyl-1,4-dibromobutane from 2,2,3,3-tetramethylbutanediol-1,4-ditosylate (MALANGA, VOGL 1983), but no dibromide was isolated when 2,3-dimethyl-2,3-dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (I) was treated in DMAc with tetra-n-butyl-

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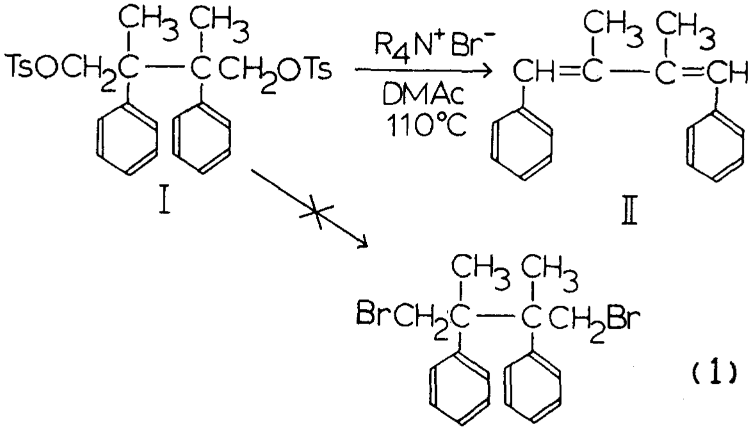
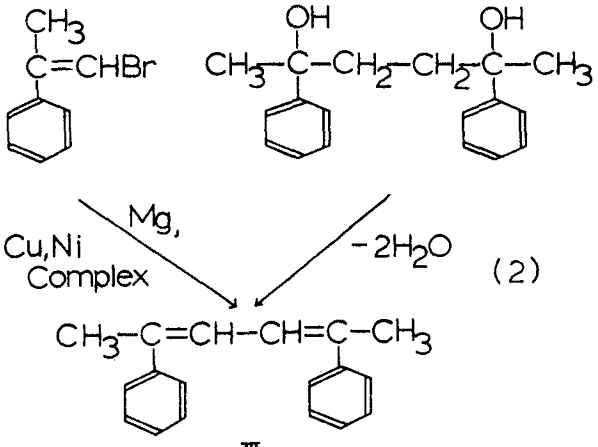


(1)

ammonium bromide (Equation 1). (I) had been prepared from methyl 2-bromo-2-phenylpropionate, which was coupled with a $CuCl_2/Zn$ reagent to dimethyl 2,3-dimethyl-2,3-diphenylsuccinate; reduction with $LiAlH_4$ to 2,3-dimethyl-2,3-diphenylbutanediol-1,4 was followed by ditosylation to (I). (I) was characterized by elemental analysis, 1-H and 13-C NMR spectroscopy. (I), as expected, was a mixture of isomers which was separated by crystallization into the meso and racemic compounds, m.p. 121°C and 170°C, respectively. We have, however, not identified yet which one of the two compounds is the meso and which is the racemic form.

Either isomer or a mixture of the two stereoisomers, when treated with tetra-n-butylammonium bromide, gave (II), m.p. 136°C (LANGER, WESSELY 1955). Only one of the three possible isomers (zz, ee or ez) was produced by this rearrangement reaction. (II) gave the correct analysis for $C_{18}H_{18}$, a proton 1-H NMR ratio of 5:3:1 at $\delta = 7.3$, 2.1 and 6.8 ppm, with a relatively sharp signal for the phenyl protons. The 13-C NMR spectrum showed peaks for CH_3 at 15.7, $=C{<}^{H}$ at 126.3, $=C{<}$ at 144.8 ppm, and the phenyl carbon atom resonances from 127 to 129 ppm. The ultraviolet spectrum of (II) showed a λ_{max} of 294 nm. (II) was synthesized from butanedione-2,3 with two mols of benzyl Grignard reagent. The initially formed 1,4-diphenyl-2,3-dimethylbutanediol-2,3 was dehydrated to (II). A mixture of the two butadienes obtained by the two different routes gave no depression of the melting point.

Another compound of a formula $C_{18}H_{18}$ that could have possibly been obtained from (I) by a more extensive rearrangement would have been 1,4-diphenyl-1,4-dimethylbutadiene-1,3 (III). This compound, would have shown by 1-H NMR spectroscopy a proton ratio of 5:3:1 and would have been obtainable in three geometric isomers (zz, ze, ez). One single isomer, a pure compound was synthesized by two different routes (Equation 2). One was by dimerization of the Grignard reagent of 1-bromo-2-phenylpropene with nickel or copper complexes and another by dehydration of 1,4-diphenyl-1,4-dimethylbutanediol-1,4



(2)

III

(FREEMAN 1957). The 1-H NMR spectrum of the compound, m.p. 139°C showed a proton ratio of 5:3:1 at $\delta=7.25$ to 7.65, 6.9 and 2.3 ppm with a broad and substantially split phenyl proton region; the 13-C NMR spectrum had chemical shift values for CH_3 at 16.2, $=\mathrm{C}{<}^{\mathrm{H}}$ at 123.9, $=\mathrm{C}{<}$ at 143.8 ppm, and the phenyl carbon atom resonance between 126 and 137 ppm. The ultraviolet spectrum of (III) had a λ_{max} at 322 nm. The melting point of a mixture of (II) and (III) had a melting point depression of over 20°C.

It appears that the rearrangement of (I) to (II) had occurred by a double 1,2 shift of the phenyl group probably via a phenonium ion rearrangement.

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