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Head-to-Head Polymers – XXXII**: Toward Head-to-Head Poly(α-Methylstyrene): Synthesis of 2,3-Dimethyl-2,3-diphenylbutanediol-1,4-ditosylate and 1,4-Diphenyl-2,3-dimethylbutadiene-1,3

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2,3-Dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (**7**) was synthesized starting from 2-phenylpropionic acid (**1**). The acid chloride was brominated and transformed into methyl 2-phenyl-2-bromo-propionate (**4**) which was coupled with a zinc/copper couple to dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (**5**). Reduction with lithium aluminum hydride to 2,3-dimethyl-2,3-diphenylbutanediol-1,4 (**6**) was followed by tosylation. The tosylate **7** a mixture of the meso and racemic compounds, could be separated into the pure isomers, **a** m. p. 170 °C and **b** m. p. 121 °C. The mixture of each individual pure compound, when treated with tetraalkyl-ammonium bromide, did not give the expected 2,3-dimethyl-2,3-diphenyl-1,4-dibromobutane (**9**) but rather 1,4-diphenyl-2,3-dimethylbutadiene-1,3 (**8**). The identity of the compound was established by independent unequivocal synthesis, the comparison of spectral characteristics, and mixed melting point.

(Keywords: Phenonium rearrangement; Nucleophilic displacement; Stereoisomers; ^{1}H- *and* ^{13}C *NMR)*

Kopf-Kopf-Polymere, XXXII. Synthese von 2,3-Dimethyl-2,3-diphenylbutandiol-1,4-ditosylat und 1,4-Diphenyl-2,3-dimethyl-butadien-1,3 mit Zielrichtung auf Kopf-Kopf-Poly(α-methylstyrol)

Ausgehend von 2-Phenylpropionsäure (**1**) wurde 2,3-Dimethyl-2,3-butandiol-1,4-ditosylat (**7**) symthetisiert. Das Säurechlorid wurde bromiert und zu Methyl-2-phenyl-2-brom-propionat (**4**) umgesetzt, das mit Zink/Kupfer zu Dimethyl-2,3-dimethyl-2,3-diphenylsuccinat (**5**) gekuppelt wurde. Reduktion mit *LAH* zu 2,3-Dimethyl-2,3-diphenylbutandiol (**6**) und nachfolgende Tosylierung ergab eine Mischung der meso und racemischen Tosylate **7 a** und **b**, welche in die reinen

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** Part XXXI: *O. Vogl*, J. Macromol. Sci., Chem., in press.

Isomere aufgetrennt werden konnten (**a** Fp. 170 °C und **b** Fp. 121 °C). Die beiden Verbindungen ergaben bei Behandlung mit Tetraalykylammoniumbromid nicht das erwartete 2,3-Dimethyl-2,3-diphenyl-1,4-dibrombutan (**9**), sondern 1,4-Diphenyl-2,3-dimethyl-butadien-1,3 (**8**). Das wurde durch unabhängige Synthese von **8** auf anderem Wege, Vergleich der spektroskopischen Eigenschaften und mittels Mischschmelzpunkt nachgewiesen.

Introduction

In the last few years a considerable amount of effort has resulted in a rather extensive understanding of the properties and the behaviour of pure head-to-head (H – H) polymers[1]. More recently, progress has been made in the preparation of H – H polymers where monomer units are disubstituted on one carbon atom. H – H polyisobutylene (*PIB*) of moderate molecular weight has been synthesized by *Grignard* coupling of 2,2,3,3-tetramethyl-1,4-dibromobutane[2,3]. The polymer properties[4] were studied and the degradation behaviour of H – H *PIB* investigated[5].

For the synthesis of H – H *PIB* methyl 2-bromoisobutyrate was coupled with a zinc/copper couple and the resulting dimethyl 2,2,3,3-tetramethylsuccinate reduced to 2,2,3,3-tetramethylbutanediol-1,4, which was tosylated. The ditosylate was treated with tetramethylammonium bromide in dimethylacetamide and 2,2,3,3-tetramethyl-1,4-dibromobutane was obtained in over 60% yield.

It was believed that this sequence of reactions could be applied starting from methyl 2-phenyl-2-bromopropionate (**4**) to prepare 2,3-dimethyl-2,3-diphenyl-1,4-dibromobutane (**9**) which would then be coupled using the *Grignard* route to give H – H poly(α-methylstyrene)[6].

H – H poly(α-methylstyrene) was of interest not only for the study of its properties and degradation behaviour but, even more importantly, for its NMR spectroscopic possibilities. It should be possible to start the polymerization with pure *meso*- or *racemic*-2,3-diphenyl-1,4-dibromobutane (**9 a, b**) which upon stereospecific polymerization would give the all *erythro* or all *threo* polymers.

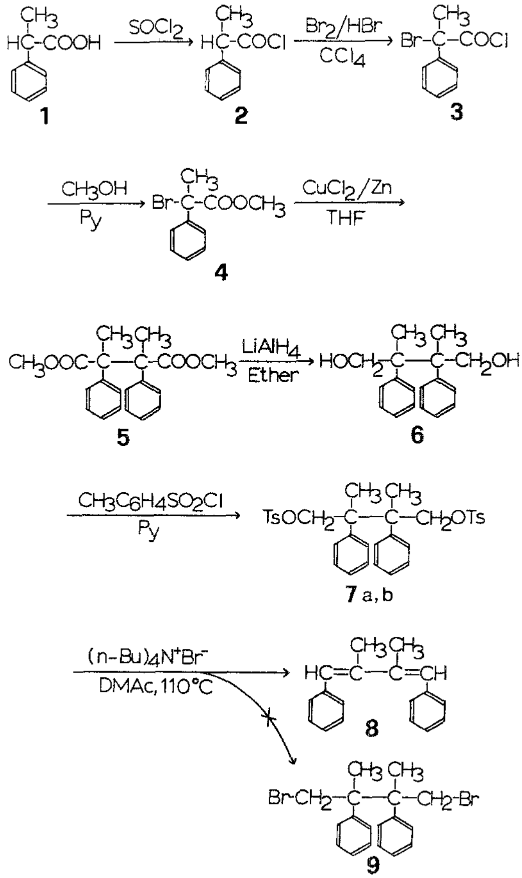
In our preliminary note we showed that the ditosylate **7** could be prepared, but nucleophilic displacement reaction actually produced 1,4-diphenyl-2,3-dimethylbutadiene-1,3 (**8**)[7].

Results and Discussion

2,3-Dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (**7**) was synthesized in a sequence of six steps. Most of the steps were similar to those that had originally been worked out for the synthesis of 2,2,3,3-butanediol-1,4-ditosylate which had earlier been developed for the synthesis of 2,2,3,3-

tetramethyl-1,4-dibromobutane, the monomer for the synthesis of H – H *PIB*.

Our starting material for the synthesis of **7** was α-phenylpropionic acid (**1**), which was allowed to react with thionyl chloride and gave the chloride **2** in over 90% yield. Bromination gave **3**, possibly in admixture with some



acyl bromide, in nearly quantitative yield. The sequence of the three steps from **1** to **4** had an overall yield of about 70%. The latter was coupled in the usual way with a zinc/copper couple to dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (**5**) in 80% yield; which was reduced with *LAH* in 78% yield to 2,3-dimethyl-2,3-diphenyl-butanediol-1,4 (**6**). Like methyl 2,3-dimethyl-2,3-diphenylsuccinate it is a mixture of the two isomers the *threo* and the *erythro* forms, which were, however, not separated at this step.

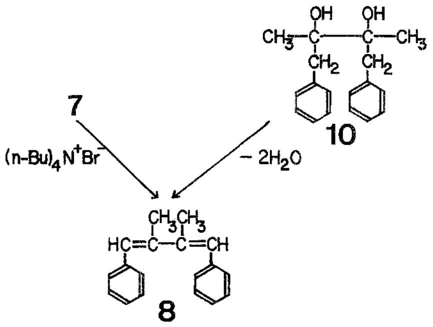
A rather simple separation of the two stereoisomers was discovered when the mixture of the stereoisomeric diols **6** was tosylated. Work-up after the first tosylation gave one of the two isomers **7a** in 46% yield, m. p. 170–171 °C. Retosylation of the mother liquors gave the other isomer (**7b**), m. p. 121–122 °C, in 20% yield.

Attempts to convert the ditosylate **7** to the dibromide by nucleophilic displacement reaction were carried out under the conditions that had been found optimum for the reaction of 2,2,3,3-tetramethylbutanediol-1,4-ditosylate to 2,2,3,3-tetramethyl-1,4-dibromobutane: Freshly prepared anhydrous tetra-*n*-butylammonium bromide in *DMAc*. The decrease and ultimately the disappearance of **7b** was monitored by NMR spectroscopy. After the reaction was complete, the reaction mixture was worked up; from the oily reaction product 35% of white crystals, m. p. 134–136 °C, could be isolated. From **7a** and tetra-*n*-butylammonium bromide the same compound was isolated (**8**). Changing of the reaction conditions or reagents (lithium bromide instead of the ammonium bromide) did not alter the yield significantly, nor did it change the type of the reaction product.

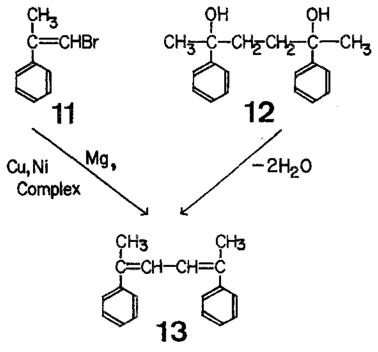
Treatment of either **7a** or **7b** with 1.3 *M* tetra-*n*-butylammonium bromide in *DMAc* at 110 °C gave a white crystalline hydrocarbon, m. p. 134–136 °C, as the sole isolable product. The elemental composition was consistent with an empirical formula C_nH_n, and if there was no overall change in the carbon skeleton of the compound (aside from a possible rearrangement), this formula was $C_{18}H_{18}$. A ^{1}H NMR spectrum exhibited singlets for aromatic hydrogens at δ 7.3, $=CH-$ at 6.8 and $=C-CH_3$ at 2.1 ppm in the ratio of 5 : 1 : 3. Absence of observable spin-spin coupling eliminates the partial structure $=CH-CH_3$. The ^{13}C NMR spectrum exhibited methyl (15.7 ppm, q), $=CH-$ (126.3 ppm, d) and $=C-$ (144.8 ppm, s) as well as aromatic carbon signals in the range 127–137 ppm. Some rearrangements must have taken place in addition to the loss of two elements of *p*-toluenesulfonic acid and 1,4-diphenyl-2,3-dimethylbutadiene-1,3 (**8**) or possibly 2,5-diphenyl-2,4-hexadiene (**13**) were the possible structures of our compound, m. p. 134–136 °C.

8 was synthesized by dehydration of 1,4-diphenyl-2,3-dimethylbutanediol-2,3 (**10**) which in turn was synthesized by a double benzyl *Grignard* reaction on 2,3-butanedione.

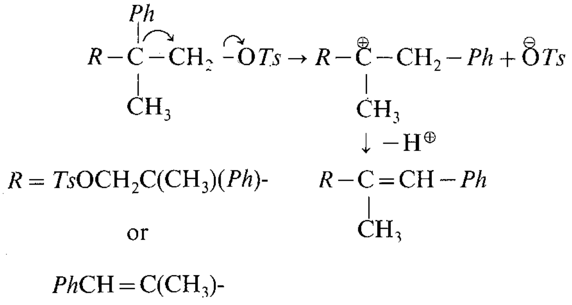
The IR, ^{1}H, and ^{13}C NMR spectra and the UV spectrum (λ_{max} of 294 nm) of **8** were identical with those exhibited by our reaction product from the detosylation of **7**. In addition, the mixed melting point of the two compounds showed no depression. A mixture of both compounds showed ^{1}H NMR spectra identical to either of the single compounds. Compound **13** (2,5-diphenylhexadiene-2,4), m. p. 138–139 °C, was synthesized by two routes: dimerization of the *Grignard* reagent of **11** with copper or nickel complexes or by dehydration of 2,5-diphenylhexanediol-2,5 (**12**). This compound had been obtained by a double *Grignard* reaction of phenylmagnesium bromide on hexadione-2,5. **13**, although also having a 5 : 1 : 3 proton ratio in its ^{1}H NMR spectrum, exhibited slightly different ^{1}H and ^{13}C NMR chemical shifts than **8** and had a λ_{max} in the UV of 322 nm. When this compound was mixed in about equal amounts with our compound and the ^{1}H NMR spectrum was taken, the spectrum showed clearly the elements of both spectra. The mixed melting point of the compounds was 114–118 °C, with a depression of about 20 °C, clearly showing that these two compounds were different.



There is also the possibility that more than one geometric isomer might be formed during the detosylation reaction. The NMR spectra are consistent with isomerically pure products possessing identical configurations about the two diene double bonds being formed in all our syntheses of the substituted dienes, including the rearrangement product 1,4-diphenyl-2,3-dimethyl butadiene-1,3 (**8**).



Formation of **8** requires 1,2-migration of phenyl groups as shown below.



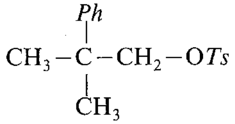
$$R-\overset{Ph}{\underset{CH_3}{C}}-CH_2-OTs \rightarrow R-\overset{\oplus}{\underset{CH_3}{C}}-CH_2-Ph + \overset{\ominus}{O}Ts \xrightarrow{-H^{\oplus}} R-\underset{CH_3}{C}=CH-Ph$$

$R = TsOCH_2C(CH_3)(Ph)$-

or

$PhCH=C(CH_3)$-

2,3-Dimethyl-2,3-diphenylbutane-1,4-ditosylate (**7**) is a close structural analog of neophyl tosylate (**14**).



$$CH_3-\overset{Ph}{\underset{CH_3}{C}}-CH_2-OTs$$

14

Owing to the steric effect of an adjacent quaternary center, bimolecular displacement of tosylate (S_N2 pathway) will be very slow[12]. There is broad agreement that neophyl tosylate **14** ionizes with phenyl bridging and with no competition from solvent-assisted pathways[13-20]. Bromide ion in the polar aprotic solvent dimethylacetamide is a powerful nucleophile. Our results make it clear that this is not sufficient to increase the rate of an intrinsically slow bimolecular pathway to the point that it competes with unimolecular ionization with phenyl bridging.

Acknowledgments

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Experimental Part

Tetrahydrofuran (*THF*) (Fisher Scientific Co.) and *N,N*-dimethylacetamide (Aldrich Chemical Co.) (*DMAc*) were purified by heating them to reflux with excess lithium aluminum hydride or phosphorous pentoxide, respectively, for two days and then distilling them under nitrogen.

Pyridine (Aldrich Chemical Co.) was distilled under reduced pressure from potassium hydroxide.

Zinc powder (Fisher Scientific Co.) was activated by washing it with a 2.5% hydrochloric acid solution for about one minute, then collecting it and washing it several times with distilled water, twice with ethanol, and once with diethyl ether. The powder was then dried at 100 °C/1 mm.

Copper(II) chloride (Fisher Scientific Co.) was obtained as the dihydrate; it was dehydrated at 100 °C for two days in vacuum (0.1 mm) prior to use.

Bromine (Aldrich Chemical Co.) was dried by shaking it with an equal volume of concentrated sulfuric acid and allowing it to stand overnight.

Methanol (Aldrich Chemical Co.) was dried by refluxing it with magnesium turnings and then distilling it under nitrogen.

Thionyl chloride (Fisher Chemical Co.) was distilled before use.

Carbon tetrachloride, *p*-toluenesulfonyl (Fisher Chemical Co.), lithium aluminum hydride (Alpha Research Chemicals and Materials) (*LAH*), *n*-butylbromide (Eastman Organic Chemicals), phosphorus oxychloride (Baker Chemical Co.), α-phenylpropionic acid, tri-*n*-butylamine, benzyl chloride, acetic anhydride, acetic chloride, bromobenzene and acetonylacetone (Aldrich Chemical Co.) were used as received.

1-Bromo-2-phenyl-propene (**11**) was synthesized according to an established procedure from α-methylstyrene (Eastman Organic Chemicals)[8].

Copper(I) tris(triphenylphosphino) bromide [Cu(I)Br(P*Ph*$_3$)$_3$] was prepared from triphenylphosphine (Aldrich Chemical Co.) and copper(II) bromide (Baker Chemical Co.)[9].

Infrared spectra were recorded on a Perkin-Elmer Model 727 spectrophotometer. Solid samples were measured as KBr pellets, liquid samples as smears between NaCl plates. The ^{1}H NMR spectra were measured on a 60 MHz Hitachi Perkin-Elmer R-24 Spectrometer using 10 to 15% solutions in $CDCl_3$ at room temperature with *TMS* as the internal standard. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer under complete proton decoupling. Melting points were measured at a rate of temperature increase of 2 °C/min and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

α-Phenylpropionyl chloride (**2**)

Thionyl chloride (124 g, 1.04 mol) was heated to reflux and α-phenylpropionic acid (77 g, 0.51 mol) was added dropwise over a period of 2 h. After addition was completed, reflux was continued for 3 h. Most of the unreacted thionyl chloride was removed under reduced pressure using an aspirator, and the residue was then distilled under reduced pressure. The major fraction distilled at a b. p. of 75–77 °C/4.5 mm; yield 92% (82.4 g). ^{1}H NMR ($CDCl_3$): $\delta = 1.55$ (*Me*), 3.95 ($>CH-$), 7.2 ppm ($-C_6H_5$). ^{13}C NMR ($CDCl_3$): $\delta = 18.7$ (*Me*); 57.4 ($>C<$); 127.9, 128.1, 129.0, 137.4 ($-C_6H_5$); 175.4 ppm ($>C=O$).

α-Bromo-α-phenylpropionyl chloride (**3**)

Into a 500 ml, 3-neck, roundbottom flask equipped with a magnetic stirring bar, reflux condenser, dropping funnel, and a nitrogen inlet and exit was placed α-phenylpropionyl chloride (82 g, 0.49 mol), and carbon tetrachloride (300 ml). With stirring, dry hydrogenbromide gas was introduced for 1 h to saturate the solution;

the solution was then heated to about 80 °C. Elemental bromine was then added dropwise very slowly over a period of nearly two days. After the addition of bromine was completed, hydrogenbromide gas was added for 4 more hours, and the reaction mixture was maintained at 80–85 °C for three more days. Carbon tetrachloride was removed, and the residue was distilled under reduced pressure giving light yellow colored α-bromo-α-phenylpropionyl chloride, b.p. 82–87 °C/0.02–0.04 mm; yield 97% (117 g). ^{1}H NMR ($CDCl_3$): $\delta = 2.35$ (*Me*), 7.3 ppm ($-C_6H_5$). ^{13}C NMR ($CDCl_3$): $\delta = 30.9$ (*Me*); 71.6 ($>C<$); 127.3, 128.4, 128.9, 129 ($-C_6H_5$); 168.4 ppm ($>C=O$).

Methyl α-bromo, α-phenylpropionate (**4**)

Into a 100 ml, 3-neck, roundbottom flask equipped with a dropping funnel, thermometer, gas inlet and exit tube, and a calcium chloride drying tube was placed methanol (150 ml, 4.8 mol) and pyridine (113 ml, 1.43 mol). This solution was cooled with an ice-salt bath to 0 °C, and α-bromo-α-propionyl chloride (117 g, 0.47 mol) was added dropwise over a period of 1 h so that the reaction was kept below 5 °C. This solution was then stirred for an additional 6 h at 0 °C and kept in a refrigerator overnight. The solution was poured into a mixture of ice (800 g) and water (200 g) and acidified with concentrated hydrochloric acid. The mixture was then extracted with two parts of ether (2 × 400 ml) and the ether solution was washed with 5% sodium bicarbonate solution (800 ml) and twice with distilled water. The ether solution was dried with anhydrous magnesium sulfate overnight and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Methyl α-bromo, α-phenylpropionate (b. p. 74–79 °C/0.02–0.04 mm) was collected in a yield of 76% (87 g). IR (neat): 1740 cm^{-1} (ν C=O). ^{1}H NMR ($CDCl_3$): $\delta = 2.2$ (*Me*), 3.6 (O*Me*), 6.9–7.5 ppm ($-C_6H_5$). ^{13}C NMR ($CDCl_3$): $\delta = 31.4$ (*Me*); 53.5 (O*Me*); 61.7 ($>C<$); 126.7, 128.4, 141.0 ($-C_6H_5$); 171.4 ppm ($>C=O$). Analysis: Calcd. for $C_{10}H_{11}O_2Br$: C 49.41, H 4.56, Br 32.87. Found: C 48.96, H 4.44, Br 33.35.

Dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (**5**)

Into a one liter, 3-neck, roundbottom flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel freshly distilled *THF* (500 ml) was added under dry nitrogen flow. Anhydrous copper(II) chloride (20 g, 0.15 mol) was added to the flask with vigorous stirring. Activated Zn powder (9.8 g, 0.15 mol) and a catalytic amount of mercuric bromide were added to the mixture. Methyl α-bromo, α-phenyl-propionate (18 g, 0.074 mol) was placed in the dropping funnel and slowly added to the mixture over a period of 20 min. After the addition of the methyl α-bromo, α-phenylpropionate was completed, the mixture was brought to reflux for 6 h, then left overnight at room temperature. After filtration, the filtrate was evaporated under reduced pressure using a rotary evaporator.

Ether (150 ml) was added to dissolve the residue, and the solution was washed with water. The ether solution was separated, dried with anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator under reduced pressure. Dimethyl 2,3-dimethyl-2,3-diphenylsuccinate was distilled at 0.02–0.04 mm at 60 °C; yield 80% (11.0 g). IR (neat): 1730 cm^{-1} (ν C=O). ^{1}H NMR ($CDCl_3$): $\delta = 1.6$, 1.7 (*Me*), 3.6 (O*Me*), 6.5–7.3 ppm ($-C_6H_5$). ^{13}C NMR ($CDCl_3$): $\delta = 22.87$, 21.98 (*Me*); 57.08, 57.31 (O*Me*); 51.86, 52.01 ($>C<$); 175.17 ($>C=O$); 126.57, 126.76, 127.28, 128.62, 128.86, 129.35, 140.04, 140.26 ppm ($-C_6H_5$). Analysis: Calcd. for $C_{20}H_{22}O_4$: C 73.60, H 6.79. Found: C 73.46, H 7.00.

2,3-Dimethyl-2,3-diphenylbutanediol-1,4 (**6**)

LAH (2.6 g, 0.068 mol) was placed in a 250 ml, 3-neck, roundbottom flask equipped with a mechanical stirrer and a dropping funnel and dissolved in anhydrous diethyl ether (80 ml). Dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (11 g, 0.034 ml) in 40 ml of anhydrous diethyl ether was added dropwise under nitrogen to the *LAH* solution over a period of 1 h while the reaction mixture was cooled in an ice bath. After the addition was complete, the reaction mixture was heated to reflux for 1 h. The mixture was allowed to cool in an ice bath and a 15% sodium hydroxide solution (3 ml) was added dropwise to the cooled mixture with vigorous stirring followed by 12 ml of water. The mixture was stirred for one h; the white solid which had precipitated was filtered and the solid extracted with several portions of ether. The ether solution was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator under reduced pressure. **6** was obtained as a white powder; yield 78% (7.1 g), m.p. 135–137 °C. IR (neat): 3300 cm^{-1} (νOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.3$ (*Me*), 1.85 ($-OH$), 3.4–4.1 ($-CH_2-$), 6.5–7.2 ppm ($-C_6H_5$). ^{13}C NMR ($CDCl_3$): $\delta = 19.64$ (*Me*); 66.96, 67.31 ($-CH_2-OH$); 48.56 and 48.86 ($>C<$); 126.37, 127.51, 128.56, 128.84, 141.77, and 142.04 ppm ($-C_6H_5$). Analysis: Calcd. for $C_{18}H_{22}O_2$: C 79.96, H 8.20. Found: C 79.96, H 8.36.

2,3-Dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (**7a, b**)

The preparation was carried out by placing 45 ml of freshly distilled pyridine into a 200 ml flask and dissolving 2,3-dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (7.0 g, 0.026 mol). The flask was placed into an ice-salt bath at − 5 °C and allowed to cool for 1 h. A magnetic stirring bar was placed in the solution and the mixture was stirred while *p*-toluenesulfonyl chloride (12.5 g, 0.066 mol) was slowly added over a period of one h. The solution was kept well agitated for the next 12 h and held at − 5 °C in the ice-salt bath. Distilled water (5 ml) was added slowly to the reaction flask with continued cooling and stirring. Distilled water (50 ml) was then added to precipitate the ditosylate; after dissolving the semisolid in methanol (100 ml), the flask was cooled in an ice bath. A white powdery product (**a**) had precipitated which was collected by filtration and dried at 0.1 mm and 60 °C overnight; yield 46% (6.9 g). The filtrate was evaporated to dryness using a rotary evaporator. The residue was allowed to react again with *p*-toluenesulfonyl chloride (6 g, 0.031 mol) using the same procedure as described above. Additional product (**b**) was obtained as a white powder; yield 20% (3.0 g) (total yield of ditosylates **a** and **b** 66%), m.p. (**a**) 170–171 °C, m.p. (**b**) 121–122 °C. Analysis: Calcd. for $C_{32}H_{34}O_6S_2$: C 66.41, H 5.92, S 11.08. Found: (**a**) C 66.35, H 5.99, S 11.07; (**b**) C 66.34, H 5.81, S 11.00. ^{1}H NMR ($CDCl_3$), (**a**): $\delta = 1.25$ (*Me*), 3.9–4.4 ($-CH_2-$), 2.3 ($-C_6H_4-CH_3$), 6.2–7.5 ($-C_6H_5$). (**b**): $\delta = 1.3$ (*Me*), 4.05 ($-CH_2-$), 2.3 ($-C_6H_4-CH_3$), 6.3–7.5 ppm ($-C_6H_5$); ^{13}C NMR ($CDCl_3$), (**a**): $\delta = 19.68$ [$>C(Me)-$]; 21.64 ($-C_6H_4-Me$); 47.33 ($>C<$); 73.98 ($-CH_2-O-$); 126.91–144.86 ($-C_6H_5$ and $-C_6H_4-$); (**b**): $\delta = 19.93$ ppm [$>C(Me)-$]; 21.62 ($-C_6H_4-Me$); 47.01 ($>C<$); 73.80 ($-CH_2-O-$), 126.89–144.83 ppm ($-C_6H_5$ and $-C_6H_4-$).

Attempted Synthesis of 2,3-Dimethyl-2,3-diphenyl-1,4-dibromobutane (**9**)

(a) Synthesis of tetra-n-butylammonium bromide: Tri-*n*-butylamine (66 g, 0.35 mol), *n*-butylbromide (49 g, 0.35 mol), and acetonitrile (32 ml) were charged into a 500-ml flask. With stirring, the mixture was heated to reflux for one day.

After the reaction was completed, the acetonitrile was removed using an aspirator. The reaction mixture was allowed to cool to room temperature and ethyl acetate (140 ml) was added. After cooling in an ice bath, a flaky, white crystalline solid was collected, which was washed with six 50-ml portions of ether, dried at 0.1 mm and 60 °C overnight. The yield of anhydrous tetra-*n*-butylammonium bromide was 80% (89 g), m.p. 104–105 °C.

(b) Reaction of bromide with 2,3-dimethyl-2,3-diphenylbutanediol-1,4-ditosylate (**7**): In a 50-ml, 3-neck, roundbottom flask equipped with a magnetic stirring bar, condenser, thermometer, and nitrogen inlet and exit was placed **7 b** (2.8 g, 0.0048 mol) and a solution of tetra-*n*-butylammonium bromide (6.3 g, 0.02 mol) in *DMAc* (15 ml). The reaction was kept under nitrogen and stirred while it was slowly heated to 110 ± 1 °C. A thermowatch temperatur monitor was used in conjunction with an oil bath to keep the temperature within one degree of 110 °C. Tosylate concentration was monitored using ^{1}H NMR spectroscopy. After reaction was carried out for 3 days, the ditosylate had disappeared; the reaction was, however, allowed to continue for another day. After cooling to room temperature, the solution was poured into 80 ml of distilled water. A viscous, oily product precipitated which was collected and washed with a small amount of acetone. A white powder separated and was collected; the yield was 0.4 g (35%); m.p. 134–136 °C. Elemental analysis (C 92.17, H 7.72) showed that there was no bromine present in the product and the compound had a basic formula of C_nH_n. A ^{1}H NMR ratio of 5 : 3 : 1 was found with ^{1}H NMR chemical shift values at $\delta = 7.3$ ppm ($-C_6H_5$), 2.1 ppm ($-CH_3$), and 6.8 ppm ($=CH-$). The ^{13}C NMR spectrum showed peaks for CH_3 at 15.7 ppm, $=CH-$ at 126.3, $=C<$ at 139.1 ppm, and phenyl carbon resonances from 127 to 139 ppm. The ultraviolet spectrum showed a λ_{max} of 294 nm, the IR (KBr): 1 610 cm^{-1} ($>C=CH-$).

The same result was obtained when **7 a** was used as the starting material for the attempted reaction with bromide.

This unexpected product was ultimately proven to have the structure of 1,4-diphenyl-2,3-dimethylbutadiene-1,3 (**8**).

Bromide substitution reactions were also attempted with lithium bromide instead of tetra-*n*-butylammonium bromide as a brominating agent and with a higher ratio of tetra-*n*-butylammonium bromide to 2,3-dimethyl-2,3-diphenylbutane-1,4-ditosylate (10 : 1). In both of these two cases, the only isolated product was still **8**. The yields were 32% and 20%, respectively.

1,4-Diphenyl-2,3-dimethylbutadiene-1,3 (**8**)

8 was prepared according to Ref.[10]: *Ph*CH_2MgCl (from 47.6 g of *Ph*CH_2Cl and 10 g of Mg) in 300 ml of absolute ether was added dropwise to 10 g of 2,3-butanedione at −20 °C in 1 h with vigorous stirring. After one day at room temperature and with the usual work-up, 12 g of pure 1,4-diphenyl-2,3-dimethylbutanediol-2,3 (**10**) were obtained after recrystallization twice from *n*-hexane, m.p. 98–100 °C.

10 (2 g), acetic anhydride (16 g), and acetyl chloride (16 g) were heated to reflux for 3 h. The solution was then cooled with an ice bath. White flakes separated, and were filtered and washed with ice water. The crude product was recrystallized with 50 ml of ethanol, and 1 g of pure **8** was obtained, m.p. 134–136 °C.

2,5-Diphenylhexadiene-2,4[1,4-diphenyl-1,4-dimethylbutadiene-1,3] (**13**)

Two different routes were adopted for the preparation of **13**. One involved dimerization of the *Grignard* reagent of 1-bromo-2-phenylpropene (**11**) with nickel or copper complexes while the other required dehydration of 2,5-diphenylhexanediol-2,5 (**12**).

(1) A 250-ml 3-neck, roundbottom flask was equipped with a reflux condenser, addition funnel, magnetic stirring bar, and a nitrogen inlet and exit tube. The glassware was flushed with dry nitrogen and flamed out. After cooling, magnesium turnings (1.2 g, 0.05 mol) which had been ground to expose fresh surfaces were charged into the reaction vessel. The turnings were flamed out under nitrogen flow to assure that all the moisture was removed; after cooling, 50 ml of dry ether were added. **11** (9.8 g, 0.05 mol) in 50 ml of dry ether was added dropwise over a period of 20 min with stirring. The reaction mixture was then heated to reflux for 24 h, $Cu(I)Br(PPh_3)_3$ (100 mg) or $NiCl_2 \cdot$ bipyridyl was added, and reflux was continued for another 3 h. The solution was evaporated to dryness, the residue extracted with petroleum ether, and the solution was concentrated to dryness under reduced pressure. The crude product was recrystallized from 20 ml of petroleum ether and **13** was obtained in 11% yield (0.65 g), m.p. 138–139 °C. Elemental Analysis: Calcd. for $C_{18}H_{18}$: C 92.26, H 7.74. Found: C 92.28, H 7.61.

(2) Phenylmagnesium bromide (from 81.5 g of brombenzene and 12.2 g of Mg) in 300 ml of absolute ether was cooled with an ice bath[11]. Hexanedione-2,5 (22.8 g, 0.2 mol) in dry ether (100 ml) was added dropwise with stirring over a period of 1 h. After 2 h at reflux, the mixture was worked up by treating it with 30% sulfuric acid. The ether layer was separated, washed twice with water, and evaporated to dryness. The crude product of **12** was obtained in a yield of 48 g (89%), m.p. 135–144 °C (a mixture of the stereoisomers).

The diol mixture (10.8 g, 0.04 mol) was heated to reflux with phosphorus oxychloride (10.2 g, 0.06 mol) in benzene (300 ml) for 4 h. After cooling to room temperature, the benzene solution was washed twice with 5% aqueous sodium carbonate solution and twice with water. The benzene layer was dried with anhydrous sodium sulfate overnight and evaporated to dryness. A yellowish crude product was obtained, which was recrystallized from about 100 ml of petroleum ether (b.p. 30–60 °C). This solution was cooled in an ice bath; white flakes separated and were isolated in a yield of 1.8 g (20%), m.p. 138–140 °C. The elemental analysis showed this product to have a composition of C_nH_n, probably $C_{18}H_{18}$: C 92.26, H 7.74. Found: C 91.91, H 7.72.

A second product was obtained from the filtrate of the work-up of this reaction mixture in a yield of 1.8 g (20%); it had an m.p. of 70–71 °C; according to ^1H and ^{13}C NMR spectra, this byproduct was 2,5-diphenyl-2,5-dimethyltetrafuran.

The product obtained by either method (1) or (2) had the same elemental composition of C_nH_n and melting points of 138–140 °C and 138–139 °C, respectively, and their mixed melting point was not depressed. The ^1H NMR spectra showed a proton ratio of 5 : 3 : 1 at $\delta = 7.25$ to 7.65 ppm, and 2.3 ppm, and 6.9 ppm. The ^{13}C NMR spectra had chemical shift values for CH_3 at 16.2 ppm, $=CH-$ at 123.9 ppm, $=C<$ at 143.8 ppm, and the phenyl carbon atom resonances between 126 and 137 ppm. The NMR spectra of the compounds prepared by route (1) or (2) were superimposable. The ultraviolet spectra of the compounds had a λ_{max} at 322 nm.

We therefore conclude that by both synthetic methods (1 and 2) 2,5-diphenylhexadiene-2,4 (**13**) had been synthesized.

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