Selective Preparation. 28.Preparation of 4,4'-di-t-Butyl-2,2'-di-Formyldiphenylmethane.

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Selective Preparation. 28. Preparation of 4,4′-di-*t*-Butyl-2,2′-di-Formyldiphenylmethane[1].

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Treatment of 4, 4'-di-t-butyl-2, 2'-bis (chloromethyl) diphenylmethane (3) with 2-nitropropane in the presence of sodium ethoxide afforded the corresponding diformyldiphenylmethane (2) in only 27% yield. The halogen exchange reaction of 3 with potassium iodide in refluxing acetone gave the corresponding diiodide (4) in 60% yield. When 4 was allowed to react with dimethylsulfoxide (DMSO) at 150°, 2 and unexpected compound 5 were obtained in 31 and 41% yields, respectively. A tentative mechanism of the formation of 5 was also discussed in this paper.

1. Introduction

Although selective introduction of functional groups to the 2, 2'-positions of diphenylmethane seems to be valuable for the preparation of large membered cyclic compounds, this is very difficult since the 2, 2'-positions are less reactive than the 4, 4'-positions of diphenylmethane.

We now wish to report a preparation of the titled compound (2) from 4, 4'-di-t-butyl diphenylmethane (**1**), which can be easily prepared by Friedel-Craft t-butylation of diphenylmethane.

2. Results and Discussion

The directive formylation of **1** with hexamethylenetetramine (HMA) in trifluoroacetic acid did not give any seizable amount of the desired compound 4, 4'-di-t-butyl-2, 2'-diformyldiphenylmethane (**2**).

In contrast, the oxidation of 4, 4'-di-t-butyl-2, 2'-bis (chloromethyl) diphenylmethane (**3**)[2], which was easily prepared by the chloromethylation of **1**, with 2-nitropropane in the presence of sodium ethoxide afforded the desired **2** in 27% yield. When **3** was treated with sodium iodide in refluxing acetone, the corresponding diiodide (**4**) was obtained in 60% yield.

Treatment of **4** with dimethylsulfoxide (DMSO) at 150° afforded **2** and an unexpected compound, thiepine **5** in 31 and 41% yields, respectively. The product **5** was identified with the authentic sample which[3] was previously prepared by the reaction of **3** with sodium sulfide.

$$3 + Na_2S \longrightarrow 5$$

The structure of **2** was determined by spectral data and formation of bis (2, 4-dinitrophenyl) hydrazone (**6**) of **2** since **2** is a liquid compound.

Unfortunately, mechanisms of the formation of **5** in the oxidation of **4** with DMSO is still not clear. However, a tentative reaction pathway of the formation of **5** might be proposed as the following Scheme 2.

The dimethylsulfide generated in the

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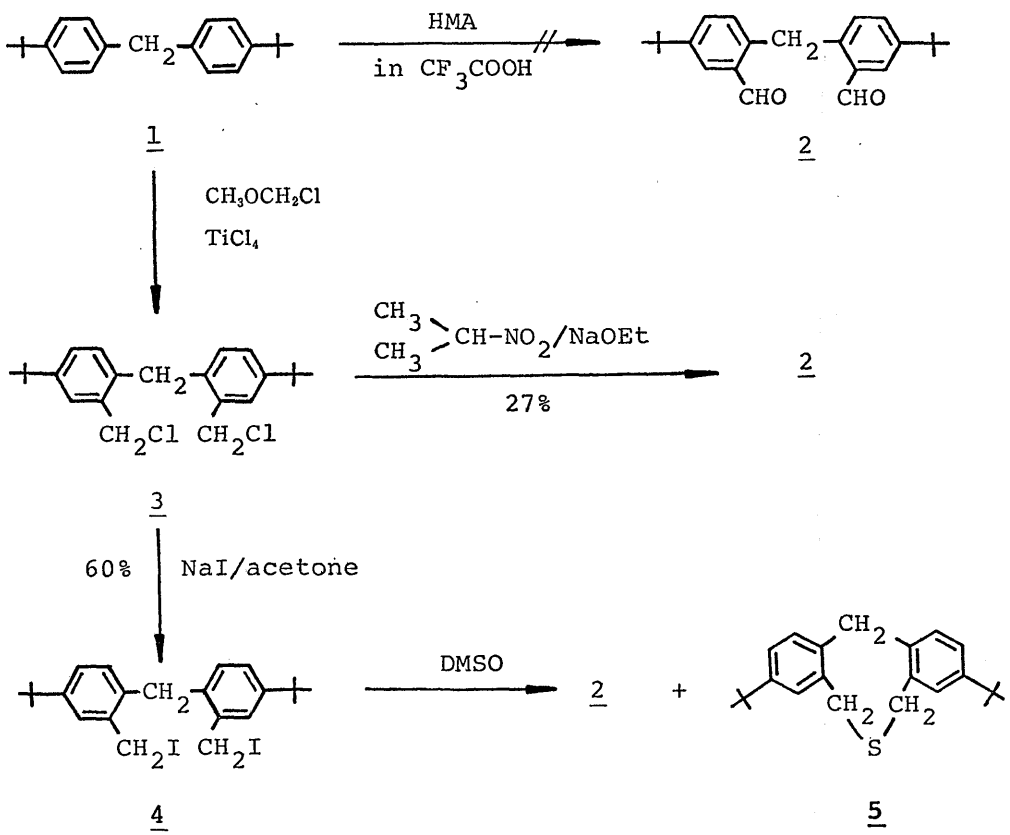
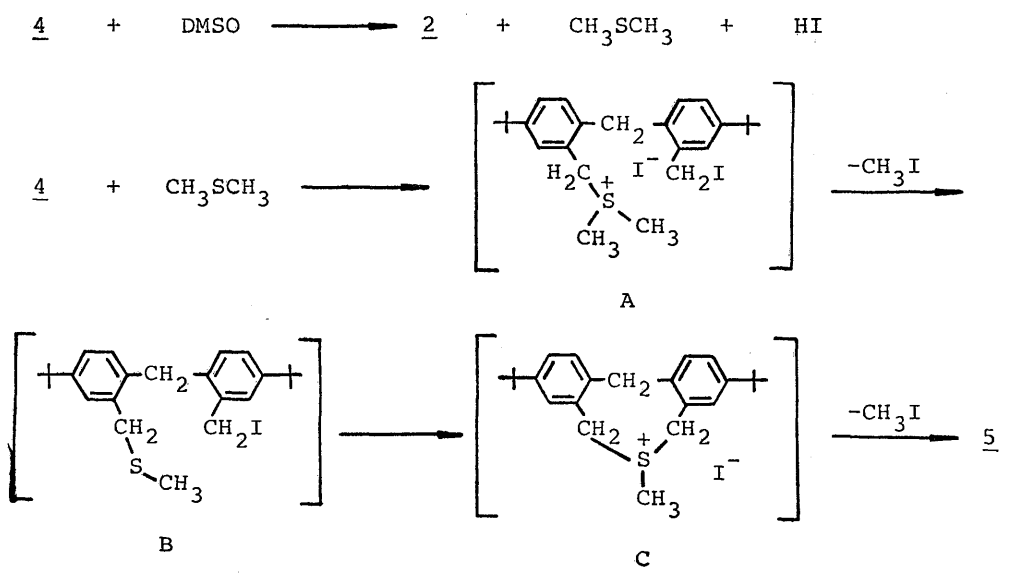


Scheme 1



Scheme 2

reaction of **4** with DMSO might react with **4** to afford the first intermediate A from which methyl iodide eliminate to give the second intermediate B. The intramolecular salt C resulting from B then releases methyl iodide again to give **5**.

3. Experimental

All melting points are uncorrected. IR spectra were measured as KBr pellets or as liquid film on NaCl plates on a Nippon Bunko IR-S spectrometer and NMR spectra were determined at 50 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal references.

Preparation of 4, 4′-*di* (*t-butyl*)-2, 2′-*di* (*iodomethyl*) *diphenylmethane* (**4**). — To a hot solution of 7.54 g (20 mmol) of **3** in 340 ml of acetone was added slowly 33.6 g of sodium iodide. After the reaction mixture was refluxed for 2 h, it was evaporated *in vacuo* to leave the residue which was washed with 300 ml of warm water and a small amount of water to give the crude product. Recrystallization of the product by ethanol afforded 6.6 g (60 %) of **3** as colorless prisms, mp 97.5–98.5°C; ir (KBr) 3060, 2960, 1500, 1360, 1150, 820, 720 cm^{-1}, pmr ($CDCl_3$) δ 1.28 (s, 18 H, t-CH_3), 4.02 (s, 2 H, CH_2), 4.38 (s, 4 H, CH_2I), 6.72–7.34 (m, 6 H, aromatic protons).

Anal. Calcd. for $C_{22}H_{20}I_2$ C 49.30 H 5.40
Found 49.57 5.43

Oxidation of 4, 4′-*di* (*t-butyl*)-2, 2′-*di* (*iodomethyl*) (**4**). — After a mixture of 2.24 g (4 mmol) of **3**, 0.84 g (10 mmol) of $NaHCO_3$ and 10 ml of DMSO was heated at 150°C for 4 min under nitrogen, it was poured into a large amount of ice-water. The organic layer was extracted with ether. The ether solution was washed with water, dried over sodium sulfate and evaporated *in vacuo* to leave the residue which was column chromatographed on silica gel using hexane and benzene as eluents to afford 0.57 g (42.2 %) of **5** from the hexane fraction and 0.42 g (31.1 %) of **2** from the benzene fraction, respectively.

2: pale yellow oil, ir (NaCl) 3040, 2960, 2570, 1695, 1505, 1360, 1200, 1070, 1030, 910, 830, 740, 690 cm^{-1}, pmr ($CDCl_3$) 1.34 (s, 18 H, t-CH_3), 4.83 (s, 2 H, CH_2), 6, 90–7.89 (m, 6 H, aromatic protons), 10.2 (s, 2 H, CHO)

2, 4-*Dinitrophenylhydrazone of* **2**. — Orange prisms (from benzene), mp 285–286°C.

Anal. Calcd. for $C_{35}H_{34}H_8O_8$
C 60.51 H 4.93 N 16.13
Found 60.69 5.14 15.85

Oxidation of 4, 4′-*di* (*t-butyl*)-2, 2′-*di* (*chloromethyl*) *diphenylmethane*.—To 30 ml of ethanol was added 0.46 g (20 mg-atom) of sodium. After the solution was cooled to room temperature, 3.0 g (34 mmol) of 2-nitropropane was added dropwise into it. To a suspension of 3.2 g (8.5 mmol) of **3** in 50 ml of DMSO was added the above prepared solution over a period of 30 min at room temperature under stirring. After the reaction mixture was stirred for further 4 h, it was poured into a large amount of ice-water, treated and worked up as described above to afford 0.78 g (27.3 %) of **2**.

References

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