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Bromination of 1,4-Diphenylbutane-1,4-dione with N-Bromosuccinimide and Bromine in Different Conditions

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The *trans*-1,2-dibenzoylethylene (**5**), 2,5-diphenylfurane (**8**), 2-bromo-1,4-diphenylbutane-1,4-dione (**4**), *cis*- and *trans*-dibenzoyl-1,2-dibromo-ethane (**6, 7**) were obtained in a one pot reaction of **3** with Br_2. The reaction of **3** with N-bromosuccinimide (NBS) gave the compounds **4** and **5**. All the isolated products by identified with NMR.

Key Words: 1,4-Diketones, 1,2-Dibenzoylethylene, Dibenzoyl-1,2-dibromoethane, 2,5-Diphenylfuran.

INTRODUCTION

1,4-Diketones are important intermediates in the synthesis of five-membered carbocyclic[1] and heterocyclic[2] compounds, including the preparation of derivatives of thiophene and other conjugated, five-membered heterocycles, which are being intensively investigated at present as monomers for electroconductive polymers[3].

The regioselective bromination of unsymmetrical ketones has attracted attention as a method to introduce functionality at the α-position. The preferred position of bromination with most brominating agents is usually at the more substituted carbon rather than at a methyl or less substituted carbon[4]. Sometimes, complex mixtures including polybrominated products are obtained. One of the well known procedures for the bromination of less substituted carbons such as methyl involves use of silyl enol ether generated from the kinetic enolate with LDA[5]. Furthermore, the 2-substitued ketones, especially, 2-phenyl ketones are used in the synthesis of a variety of biologically interesting compounds[6].

In this work, we report the brominaton of 1,4-diphenylbutane-1,4-dione in Br_2 and N-bromosuccinimide (NBS) in different conditions.

EXPERIMENTAL

All the solvents were dried and distilled by standard procedures. ^{1}H- and ^{13}C NMR spectra were recorded on 200 (50) MHz Varian spectrometers and reported in δ units with TMS as internal standard. IR spectra were recorded on a Jasco FT/IR-430 spectrometer. All column chromatography was performed on silica gel (60 meshes, Merck).

Reaction of 1,4-diphenylbutane-1,4-dione with Br_2: To a stirred solution of **2** (1 g, 4.2 mmol) in 30 mL of $CHCl_3$ was added solution of Br_2 (0.67 g, 4.2 mmol) in 10 mL of $CHCl_3$ at room temparature for 0.5 h. After stirring for 0.5 h, the mixture was washed with water (20 × 50 mL), dried over $MgSO_4$ and the solvent was removed *in vacuum* to give 1.181 g of crude product, as a viscous oil. The crude product was chromatographed over silica gel (40 g). Elution with *n*-hexane/$CHCl_3$ (7:3) gave 2,5-diphenylfuran (**8**) as the first fraction (103 mg, 11 %; white crystals from $CHCl_3$/hexane; m.p. 88-90 ºC, lit.[7] 88-89 ºC). ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.79$ (m, 4H), 7.44 (m, 4H), 7.30 (m, 2H), 6.77 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 155.43$, 132.95, 130.71, 129.35, 125.76, 109.23.

The elution with the same solvent afforded the *trans*-dibenzoyl-1,2-dibromoethane (**7**) as the second fraction (217 mg, 13 %) : white needles crystals from $CHCl_3$/*n*-hexane; m.p. 184-186 ºC, lit.[8] 185-186 ºC). ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 8.11$ (m, 4H), 7.60 (m, 6H), 5.97 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 192.59$, 136.36, 136.14, 136.10, 131.03, 43.26.

The same solvent yielded *cis*-dibenzoyl-1,2-dibromoethane (**6**) as the third fraction (421 mg, 25 %; white needles crystals from $CHCl_3$/*n*-hexane; m.p. 151-154 ºC, lit.[8] 152-154 ºC). ^{1}H NMR (200 MHz, $CDCl_3$) $\delta =$ 8.03 (m, 4H), 7.58 (m, 6H), 5.78 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta =$ 194.94, 136.18, 135.61, 130.97, 130.83, 50.85.

The same solvent gave (E)-1,4-diphenylbut-2-ene-1,4-dione (**5**) as the fourth fraction (159 mg, 16 %; colourless crystals from $CHCl_3$/*n*-hexane; m.p. 108-111 ºC, lit.[9,10] 109-110 ºC). ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.99$ (m, 4H), 7.52 (m, 6H), 6.97 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 197.74$, 137.61, 134.40, 130.66, 129.16, 115.16.

The fifth fraction is 2-bromo-1,4-diphenylbutane-1,4-dione (**4**) (281 mg, 28 %; colourless crystals from $CHCl_3$/*n*-hexane, m.p. 141-144 ºC). ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 8.25$-7.23 (m, 4H, ArH), 7.73-7.48 (m, 6H, ArH), 5.73 (dd, $J = 10.3$, 5.4 Hz, 1H, CH-Br), 4.74 (dd, $J = 19.2$, 10.3 Hz, 1H, CH_2) 3.85 (dd, $J = 19.2$, 5.4 Hz, 1H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 200.35$, 193.65, 137.85, 136.10, 135.84, 135.21, 134.73, 131.03, 129.78, 129.11, 50.38, 36.68. IR (KBr, cm^{-1}) 3064, 3023, 2952, 2923, 2852, 1675, 1594, 1444, 1344, 1288, 1218, 1172, 1012, 902, 790, 686, 520. Anal. (%) calcd. for ($C_{16}H_{13}O_2Br$): C, 60.59, H, 4.13; Found: C, 60.27, H, 3.98.

Reaction of 1,4-diphenylbutane-1,4-dione (3) with NBS: A solution of 1,4-diphenylbutane-1,4-dione (**3**) (0.2 g 0.83 mmol) in a 20 mL $CHCl_3$ was added NBS (0.15 g, 0.84 mmol) and a small amount of AIBN. The reaction mixture was heated under reflux temperature 1 h. After the mixture was cooled to room temperature, the insoluble materials were separated by filtration. The mixture was washed with water and dried over $MgSO_4$. After the solvent was removed *in vacuo* the crude product was submitted on a silica gel column and eluted with *n*-hexane. The first fraction was the 2,5-diphenylfuran (**8**) (150 mg, 83 %).

The second fraction was the 2-bromo-1,4-diphenylbutane-1,4-dione (**4**) (0.1 g, 37 %).

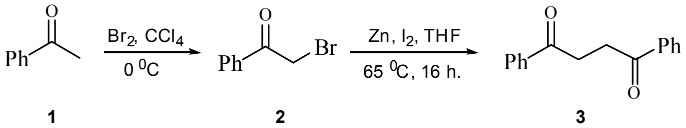
1,4-Diphenylbutane-1,4-diol (9): To a solution of 1,4-diphenylbutane-1,4-dione (**3**) (0.75 g, 3.1 mmol) in a 30 mL CH_3OH was added $NaBH_4$ (0.25 g, 6.7 mmol) for 0.5 h and stirred for 3 h at room temperature. The mixture was neutralized with 0.1 M HCl and washed with water. The organic layer was dried over Na_2SO_4. The removal of the solvent gave the mixture of distereomer of 1,4-diphenylbutane-1,4-diol (**9**) in ratio of 8:2 was removed *in vacuum*. The crude products was crystallized in *n*-hexzane/ CH_3OH (7:3) (7.4 g, 97 %, m.p. 92-94 ºC). ^1H NMR (200 MHz, $CDCl_3$) δ = 7.32-7.25 (m, aromatic, 10H), 4.70-4.65 (m, 2H), 2.82-2.80 (br. s, -OH, 2H), 1.91-1.78 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.65, 130.41, 129.45, 127.92, 76.54, 37.83, 37.12. IR (KBr, cm^{-1}) 3370, 3083, 3062, 3027, 2948, 2917, 2869, 1598, 1488, 1450, 1324, 1305, 1214, 1060, 1022, 912, 757, 701, 543.

1,4-Dibromo-1,4-diphenylbutane (10): To a solution of alcohol **3** (0.75 g, 3.06 mmol) and pyridine (0.25 g, 3.16 mmol) in 20 mL of benzene was added the solution of PBr_3 (1.3 g, 4.8 mmol) in 10 mL of benzene at 0 ºC during the 1 h. The reaction mixture was stirred at room temperature for 6 h. The mixture was filtrated for removing of insoluble materials and extracted with *n*-hexane. The organic layer was dried over $CaCl_2$. The removal of the solvent gave the 1,4-dibromo-1,4-diphenylbutane (**10**) (0.76 g, 73 %, needle crystal, m.p. 178-180 ºC). ^1H NMR (200 MHz, $CDCl_3$) δ = 7.41-7.25 (m, 10H, ArH), 4.99-4.93 (m, 2H), 2.45-2.25 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 143.57, 130.91, 130.55, 129.20, 56.27, 40.66. IR (KBr, cm^{-1}) 3058, 3023, 2929, 2857, 1494, 1450, 1305, 1214, 1006, 981, 752, 698.

RESULTS AND DISCUSSION

1,4-Diphenylbutane-1,4-dione (**3**) was synthesized according to previous reported procedure[7]. Bromination of acetophenone **1** with bromine yield ω-bromoacetophenone **2**. The treatment of ω-bromoacetophenone **2** with zinc dust in the presence of a small amount of iodine at 65 ºC gave the

1,4-diphenylbutane-1,4-dione **3**, which is Wurtz-like condensation product (**Scheme-I**).

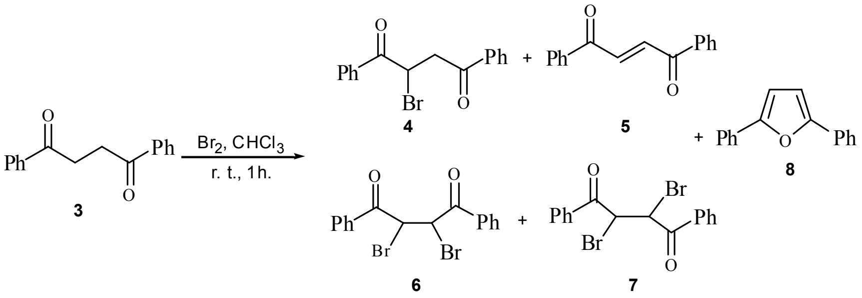


1 **2** **3**

Scheme-I

The structure of **3** was determined by spectral data which is in accord with the literature data[11].

The reaction of **3** with Br_2 in $CHCl_3$ at room temperature was surprising. The ^1H NMR studies revealed that the reaction mixture was very complex. Indeed, five products (**4-8**) were isolated after repeated and careful column chromatography (**Scheme-II**).

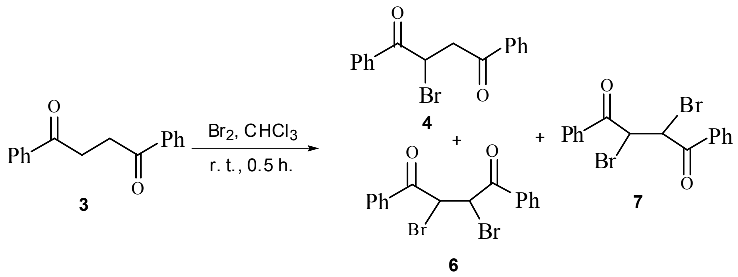


3 **4** **5** **8** **6** **7**

Scheme-II

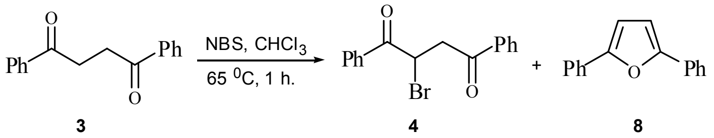
The compounds **5**[9,10], **6**[8], **7**[8] and **8**[7,12] were identified by comparison of the spectroscopic data and mp with those of authentic samples. The compound **8** was also obtained by the reaction of **3** with *p*-TsOH in THF for 72 h at reflux. The spectral data of the latter compound is in agreement with the former reaction product and literature. The structure of monobromide **4** was determined on the basis of spectral data. In ^1H NMR spectrum of **4** shows an AB system at centered 4.74 and 3.85 ppm for methylene protons. A part of AB system gives doublet of doublet (J = 19.2, 10.3 Hz) at 4.74 ppm and B part of AB system gives doublet of doublet (J = 19.2, 5.4 Hz) at 3.85 ppm. Additon, CHBr proton gives a doublet of doublet (J = 10.3, 5.4 Hz) at 5.73 ppm. These findings are in agreement with proposed structure of **4**.

When the same reaction was completed for 0.5 h, it was seen that the (E)-1,4-diphenylbut-2-ene-1,4-dione (**5**) and the 2,5-diphenylfurane (**8**) were not occurred (**Scheme-III**).



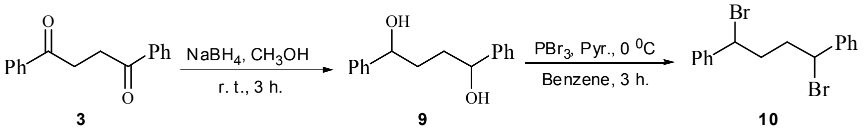
Scheme-III

Additionaly, the reaction of 1,4-diphenylbutane-1,4-dione (**3**) with NBS in $CHCl_3$ at 65 ºC for 1 h gave the only two products: 2-bromo-1,4-diphenylbutane-1,4-dione (**4**) and 2,5-diphenylfurane (**8**) (**Scheme-IV**).



Scheme-IV

In last, 1,4-diphenylbutane-1,4-dione (**3**) was reduced to the 1,4-diphenylbutane-1,4-diol (**9**) with $NaBH_4$. 1,4-Dibromo-1,4-diphenylbutane (**10**) was obtained from the reaction of 1,4-diphenylbutane-1,4-diol (**9**) with PBr_3 (**Scheme-V**).



Scheme-V

The structures of diol **9**[14] and dibromide **10**[14] were determined on basis of spectral data and comparison with literature data.

Conclusion

Bromination of 1,4-diphenylbutane-1,4-diol (**9**) with molecular Br_2 for 1 h gave the one mono brominated **4**, two dibrominated **6** and **7**, elimination **5** and rearrangement product **8**. When the same reaction was completed for 0.5 h, the products **5** and **8** were not occur. Bromination of 1,4-diphenylbutane-1,4-diol (**9**) with NBS resulted in formation of mono bromide 4 and 2,5-diphenylfuran (**8**).

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