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SUPPL.FREE-RADICAL BROMINATION OF SELECTED
ORGANIC COMPOUNDS IN WATERHenry Shaw*, Howard D. Perlmutter and Chen Gu
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SUPPLEMENTARY MATERIAL - EXPERIMENTAL

General Information. Melting points were uncorrected. FT-IR spectra were recorded on a spectrophotometer using KBr plates for neat liquids and KBr pellets for solid samples. ^1H NMR and ^{13}C NMR spectra were taken on a using CDCl_3 as solvent. Mass spectra were also taken on a Ion Trap TIC-MS spectrometer. TLC experiments were carried out on plastic-backed plates coated with 0.2-mm. silica gel while flash column chromatography was carried out using 60-100 mesh silica gel as the stationary phase. GLC analyses were performed on an instrument equipped with flame ionization detector using temperature programming. The GLC columns used were DB-WAX (30 m x 0.32 mm. ID) capillary column, Tenax TA (2 m x 1/8") packed column, and 5% SE-30 on Chromo Q (2 m x 1/8") packed column.

Materials. o-xylene, toluene, p-xylene, m-xylene, mesitylene, cyclohexane and cyclohexene obtained from Aldrich Chemical Co. were all glass-distilled before use. Diphenylmethane, triphenylmethane, durene, and bromine obtained from Aldrich were used without further purification. All other reagents obtained from Aldrich were of analytical grade.

General Procedure. A 100-cm³ three-necked round-bottomed flask fitted with mechanical stirrer, dropping funnel and condenser was used. A typical procedure consisted of adding Br₂ to a vigorously stirred aqueous suspension of either liquid or solid substrate and then irradiating with visible light (200 Watt incandescent light bulb) placed 5 cm. from the upper portion of the flask. Completion of the reaction was indicated by the complete disappearance of the Br₂ color and the appearance of three layers, the middle one being aqueous HBr. The reaction mixture was allowed to cool to room temperature. To determine the amount of HBr produced from the reaction, the aqueous layer was titrated with 0.1 M NaOH solution using phenolphthalein as indicator. The lower organic layer was washed 3 times with water to remove residual HBr, and was dried with Na₂SO₄ or MgSO₄ for at least one hour. Products were purified, if necessary, either by flash column chromatography or by repeated recrystallizations from suitable solvents. Products were identified by FT-IR, GC-MS and ¹H NMR analyses and analyzed quantitatively by GLC using external standard solutions. The upper organic layer was analyzed for 100% starting material.

1. o-XYLENE (1)

(a) In the presence of light and at room temperature. In a three-necked round-bottomed flask, fitted with mechanical stirrer, condenser and dropping funnel, were placed 1.25 cm³ (10.0 mmol) of 1 and 25 cm³ H₂O. The mixture was stirred vigorously and from a dropping funnel was added 0.52 cm³ (10.0 mmol) of Br₂. The mixture was then irradiated with visible light from an incandescent 200 Watt bulb for 20 minutes after which time complete disappearance of the bromine color was observed. After the reaction, the mixture was allowed to cool to 60°C and the aqueous layer separated. The upper organic

layer was analyzed for starting material. As the lower organic layer was cooling slowly to room temperature, a solid substance mixed with viscous liquid began to form. The crude product was GLC analyzed using DB-WAX capillary column with oven temperature programming, 60°C to 200°C and with the use of external standards. The resulting analysis gave α,α' -dibromo-o-xylene (1a, 79% yield), α -bromo-o-xylene (1b, 16% yield), 4-bromo-o-xylene (1c, 3% yield) and 3-bromo-o-xylene (1d, 2% yield) as the products.

(b). In the dark and at a temperature of 80°C. The procedure in (a) was followed except that light was eliminated from the system by wrapping the flask with aluminum foil and the mixture was heated to 80°C for 120 minutes after which time complete disappearance of the bromine color was observed. After cooling the reaction mixture to room temperature, the upper organic layer analyzed for starting material. The lower organic layer was GLC analyzed using the conditions in (a). The resulting analysis gave only ring brominated products, 4-bromo-o-xylene (1c, 84% yield) and 3-bromo-o-xylene (1d, 16% yield).

(c). In the dark and at room temperature. The procedure in (a) was followed except that the reaction was allowed to proceed in the dark and at room temperature for a period of 48 hours. Complete disappearance of the bromine color was observed after this time. The lower organic layer, separated from the aqueous layer, was GLC analyzed using the conditions in (a). The resulting analysis gave 4-bromo-o-xylene (1c, 83% yield) and 3-bromo-o-xylene (1d, 17% yield) as the products.

2. TOLUENE (2)

The set-up in 1(a) was used. To a stirred suspension of 2 (2.13 cm³, 20.0 mmol) in 50 cm³ H₂O was added Br₂ (0.52 cm³, 10.0 mmol) in one batch. The mixture was irradiated with incandescent light for 20 minutes after which time complete disappearance

of the bromine color was observed. The mixture was cooled to room temperature and the lower organic layer, separated from the aqueous layer, was washed with water to remove residual HBr and dried with Na_2SO_4 . The crude product was purified by vacuum distillation to give benzyl bromide (**2a**); 98% yield (based on bromine); ^1H NMR spectrum of **2a** was identical with the one in literature (1).

3. p-XYLENE (**3**)

The set-up in 1(a) was used. To a stirred suspension of **3** (2.45 cm^3 , 20.0 mmol) in $50\text{ cm}^3\text{ H}_2\text{O}$, was added Br_2 (1.03 cm^3 , 20.0 mmol) in one batch. The mixture was irradiated with incandescent light for 20 minutes after which time bromine color disappeared completely. After reaction, the mixture was allowed to cool to room temperature and the lower organic layer was separated from the aqueous layer. The dried lower organic layer was purified by flash column chromatography using hexane as eluant. Two products were isolated which were further purified: (a) the semi-solid product was recrystallized from acetone affording α -bromo-p-xylene (**3b**), with melting point range of $35\text{-}39^\circ\text{C}$ (lit.(2) mp 35°C) and based on **3**; (b) the crystalline product was recrystallized from hot 95% ethanol giving α,α' -dibromo-p-xylene (**3a**), with melting point range of $145\text{-}147^\circ\text{C}$ (lit.(2) mp $145\text{-}147^\circ\text{C}$) and a 80% yield (based on **3**). ^1H NMR spectra of **3a** and **3b** were identical with those in the literature (1).

4. m-XYLENE (**4**)

The set-up in 1(a) was used. To a stirred suspension of **4** (2.45 cm^3 , 20.0 mmol) in $50\text{ cm}^3\text{ H}_2\text{O}$, was added Br_2 (1.03 cm^3 , 20.0 mmol) in one batch. The mixture was irradiated with incandescent light for 20 minutes after which time bromine color disappeared completely. After reaction, the mixture was allowed to cool to room

temperature and the organic layers were separated from the aqueous layer. The upper organic layer analyzed for starting material. The lower organic layer, washed with water and dried with Na_2SO_4 , was purified by flash column chromatography using hexane as eluant. Two products were isolated which were further purified: (a) the liquid product was vacuum distilled affording α -bromo-m-xylene (**4b**), 40% yield (based on **4**) ; (b) the crystalline product was recrystallized from hot 95% ethanol giving α,α' -dibromo-m-xylene (**4a**), with melting point range of 76-77°C (lit.(2) m.p. = 77°C) and a 53% yield (based on **4**). ^1H NMR spectra of **4a** and **4b** were identical with those in the literature (1).

5. DIPHENYLMETHANE (**5**)

The set-up in 1(a) was used. To a stirred suspension of **5** (1.69 grams, 10.0 mmol) in 25 cm^3 H_2O , was added Br_2 (0.26 cm^3 , 5.00 mmol) in one batch. The mixture was irradiated with incandescent light for 10 minutes after which time the bromine color disappeared completely. After reaction, the mixture was allowed to cool to room temperature and the lower organic layer was separated from the aqueous layer. The organic layer, washed with water, dried with Na_2SO_4 , and purified by flash column chromatography using ethyl acetate-hexane (4:1) as eluant, afforded a semi-solid product which was further recrystallized from acetone giving α -bromodiphenylmethane (**5a**), melting point of 41-45°C (lit.(2) m.p. = 45°C), and a yield of 81%, which was based on GLC analysis using Tenax stainless steel pre-packed column with oven T = 300°C and with the use of an external standard. The ^1H NMR spectra of **6a** was identical with the one in literature (1).

6. TRIPHENYLMETHANE (**6**)

The set-up in 1(a) was used. To a stirred suspension of **6** (2.44 grams, 10.0 mmol) in 25 cm³ H₂O, was added Br₂ (0.26 cm³, 5.00 mmol) in one batch. The mixture was irradiated with incandescent light for 120 minutes after which time complete disappearance of bromine color was observed. After reaction, the mixture was allowed to cool to room temperature and the heavier-than-water solid product was separated from the aqueous layer. The solid product, was washed with water and then purified by repeated recrystallizations from acetone giving α -bromotriphenylmethane (**6a**), melting point range of 153-154°C (lit.(2) m.p. = 152-154°C) and a yield of 86%, which was based on GLC analysis utilizing Tenax stainless steel pre-packed column with oven T = 300°C and with the use of an external standard. The ¹H NMR spectrum of **6a** was identical with the one in the literature (1).

7. MESITYLENE (7)

The set-up in 1(a) was used. To a stirred suspension of **7** (2.8 cm³, 20.0 mmol) in 50 cm³ H₂O, was added Br₂ (0.52 cm³, 10.0 mmol) in one batch. The mixture was irradiated with incandescent light for 2 minutes after which time complete disappearance of bromine color was observed. After reaction, the mixture was allowed to cool to room temperature and the lower organic layer was separated from the aqueous layer. The organic layer was washed with water, dried with Na₂SO₄, and was purified by means of vacuum distillation affording 1-bromo-2,4,6-trimethylbenzene (**7a**), with a yield of >90% (based on bromine). The corresponding reaction in the dark (reaction time = 20 minutes) also gave 1-bromo-2,4,6-trimethylbenzene (**7a**) (>90% yield) as the product. The ¹H NMR spectrum of **7a** was identical with the one in literature (1).

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8. DURENE (8)

The set-up in 1(a) was used. To a stirred suspension of **8** (2.68 grams, 20.0 mmol) in H₂O, was added Br₂ (0.52 cm³, 10.0 mmol) in one batch. The mixture was irradiated with incandescent light for 3 minutes after which time complete disappearance of bromine color was observed. After reaction, the mixture was allowed to cool to room temperature and the solid product was separated from the aqueous layer. The solid product was washed with water and was purified by flash column chromatography using hexane as eluant; the isolated solid product was further purified by repeated recrystallizations from acetone affording 1-bromo-2,3,5,6-tetramethylbenzene (**8a**), melting point range of 59-61°C (lit.(2) m.p. = 61°C), and a yield of >90% (based on bromine). The corresponding reaction in the dark (reaction time = 3 hours) also gave 1-bromo-2,3,5,6-tetramethylbenzene (**8a**) as the product. The ¹H NMR spectrum of **8a** was identical with the one in the literature (1).

9. CYCLOHEXANE (9)

The set-up in 1(a) was used. To a stirred suspension of **9** (1.09 cm³, 10.0 mmol) in 25 cm³ H₂O, was added Br₂ (0.52 cm³, 10.0 mmol) in one batch. The mixture was irradiated with incandescent light for 20 minutes after which time complete disappearance of the bromine color was observed. After the reaction, the mixture was allowed to cool to room temperature and the upper organic and aqueous layer removed. The lower organic layer, washed with water, and dried with Na₂SO₄, was GLC analyzed using 5% SE-30 on Chrom Q packed column with oven temperature programming, 60- 120°C and with the use of external standards. The resulting analysis gave 1-bromocyclohexane (**9a**, 31%

50% 7

yield), and 1,2-dibromocyclohexane (9b, 56% yield) as the products. The corresponding reaction in the dark did not occur even for several days.

10. CYCLOHEXENE (10)

The set-up in 1(a) was used. A stirred suspension of 10 (2.03 cm³, 20.0 mmol) in 25 cm³ H₂O, was irradiated with incandescent light, and then Br₂ (1.03 cm³, 20.0 mmol) was added dropwise. The color of bromine was dissipated at once as Br₂ was being added to the mixture. After complete addition of Br₂, the mixture was allowed to cool to room temperature, and the aqueous layer decanted off. The lower organic layer was washed with water, dried with Na₂SO₄, and vacuum distilled affording trans-1,2-dibromocyclohexane (10a) as the product with a yield of >96% (based on 10). The corresponding reaction in the dark also gave 10a with a yield of >97% (based on 10). The ¹H NMR spectrum of 10a was identical with the ¹H NMR spectrum of the commercially available trans-1,2-dibromocyclohexane (1).

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