

Photochemical bromination of substituted indan-1-one derivatives: synthesis of new polybromoindan-1-one derivatives

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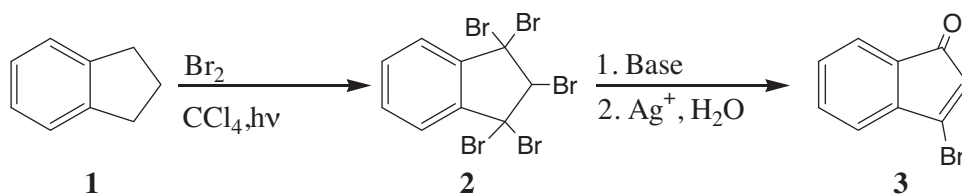
The photobromination of substituted indan derivatives was studied. Four products, 2,3-dibromo-inden-1-one (**5**), *trans*-2,3-dibromoindan-1-one (**6**), 2,2-dibromoindan-1,3-dione (**7**) and 2,2-dibromoindan-1-one (**8**), were obtained by the bromination of indan-1-one (**4**). The bromination of 2-methyl indanone (**9**) and 3-methyl-indanone (**13**) gave the corresponding monobromo, dibromo, and tribromo compounds in high yield. 4-Nitro indan (**16**) was tribrominated under same condition reaction. The structures of these products were determined from ¹H-NMR, ¹³C-NMR, MS, and IR data.

Key Words: Indan-1-one, 2-methyl-1-indanone, 3-methyl-1-indanone, 4-nitro indan.

Introduction

The bromination of hydrocarbons is an important process because it yields useful intermediates for the synthesis of a variety of bromoorganic compounds.^{1–10} These compounds have numerous industrial application as pesticides, plastics, fire retardants, and pharmaceutical chemicals.¹¹

An indenone motif can be found in some natural products and also in synthetically obtained compounds.^{12–15} Several procedures for the synthesis of indenones have been reported in the literature.^{16–24} Photochemical bromination of indan **1** gave the bromo indenone,³ which can serve as the key compound for the construction of a benzo[*c*]fluorenone skeleton (Scheme 1).¹⁶



Scheme 1

In this paper, we describe a method for the synthesis of brominated indenone derivatives, which can serve as the key compounds for the preparation of other substituted indenone derivatives. The work presented is a continuation of the current interest in the photochemical bromination reaction of indane derivatives.¹⁶

Experimental

All chemical reagents were commercially available. The substrates were purified (distilled or crystallized) before application in the reaction. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400-100 MHz spectrometer. Infrared spectra were obtained as films on NaCl plates for liquid and KBr pellets for solids on a Win First®Satellite Model infrared recording spectrophotometer. All column chromatography was performed on silica gel (60-mesh, Merck).

General procedure for photobromination

All bromination reactions were carried out in a cylindrical vessel with 2 necks attached to a Dimroth cooler and dropping funnel. In the photobromination reactions, a 150 W projector lamp provided the internal irradiation.

Photobromination of 1-indanone (4)

A solution of bromine (14.8 mmol, 2.36 g) in CCl₄ (10 mL) was added dropwise over 30 min to a stirred solution of indan-1-one (4) (500 mg, 3.7 mmol) in CCl₄ (60) in a photochemical reaction apparatus with irradiation by 150 W projector lamp. After completion of the reaction (60 min), the excess of bromine and the solvent were removed at reduced pressure at 35 °C. The dark residue was crystallized from chloroform to give 2,2-dibromo-1-indanone (8). After filtration of 8, the organic solvent was evaporated and oily residue was chromatographed on silica gel (130 g), eluting with hexane/chloroform (1/4). The first fraction consisted of a mixture of 5 and 6. This mixture was submitted to fractional crystallization from chloroform to give 5 and 6. From the second fraction, dibromo indandione 7 was isolated.

2,3-dibromoinden-1-one (5)¹⁶: 400 mg 39%, red crystals, mp 125 °C (Lit. 123 °C)

trans-2,3-dibromoindan-1-one (6)^{26,27}: 100 mg, 10%, red viscous liquid,

2,2-dibromoindan-1,3-dione (7)²⁸: 200 mg, 18%, colorless crystals, mp 183-185 °C (Lit. 181-182 °C)

2,2-dibromoindan-1-one (8): 150 mg, 15%, colorless crystals, mp 140-142 °C, (Found: C, 37.25, H, 2.08, C₉H₆Br₂O requires C: 37.28, H: 2.09 MS *m/z* (M⁺), 292, 290, 288 (M⁺, -Br), 211, 208 (M⁺, -Br), 131, 130, 129, (M⁺, -C=O), 103, 102, 101, IR (KBr, cm⁻¹) 1716 (-C=O).

Photobromination of 2, 3-dibromo-inden-1-one (5)

Fifty milligrams (0.18 mmol) of **6** was dissolved in 15 mL of carbon tetrachloride. The reaction was carried out as described above. The solvent was evaporated and residue crystallized from chloroform to give 50 mg (95%) of dibromo indandione **7**.

Photobromination of 2-methyl indanone (9)

A solution of bromine (13 mmol, 2.13 g) in CCl₄ (10 mL) was added dropwise over 30 min to a stirred solution of 2-methyl indanone (**9**) (500 mg, 3.4 mmol) in CCl₄ (60) in a photochemical reaction apparatus with irradiation by 150 W projector lamp. After completion of the reaction (60 min), the excess of bromine and the solvent were removed at reduced pressure at 35 °C. The oily residue was chromatographed on silica gel (130 g), eluting with hexane/chloroform (1/4), and the fractions were crystallized from chloroform.

2,3,3-tribromo-2-methyl-indan-1-one (**10**) 700 mg, 53%, yellow crystals, mp 115-117 °C, (Found: C 31.34, H 1.95, C₁₀H₇Br₃O requires C 31.37, H 1.84%), MS *m/z* 305, 303, 301 (M⁺, -Br), 224, 222, 221 (M⁺, -Br), 144, 143, 142 (M⁺, -Br), 116, 115, 114 (M⁺, -C=O) IR (KBr, cm⁻¹) 1723 (-C=O).

2,3-dibromo-2-methyl-indan-1-one (**11**) 155 mg, 20%, pale yellow crystals, mp 110-111 °C, (Found: C 39.49, H 2.63, C₁₀H₈Br₂O requires C 39.51, H 2.65%), MS *m/z* 225, 223, 221 (M⁺, -Br), 145, 143, 142 (M⁺, -Br), 116, 115, 114 (M⁺, -CO), IR (KBr, cm⁻¹) 1806 (-C=O)

2-Bromo-2-methyl-indan-1,3-dione (**12**) 56 mg, 20%, pale yellow crystals, mp 210 °C, (Found: C 50.25, H 2.90% requires C 50.24, H 2.95%), MS *m/z* 176 (M⁺, -CO, -CH₃), 133 (M⁺, -CO), IR (KBr, cm⁻¹) 1709 (-C=O).

Photobromination of 3-methyl indanone (13)

To 500 mg (3.4 mmol) of 3-methyl indanone (**13**) was added dropwise over 30 min 2.31 g (13 mmol) of bromine while the reaction flask was irradiates with a 150 W projector lamp. After completion of the reaction (130 min), the excess of bromine and the solvent were removed at reduced pressure at 35 °C. The organic solvent was evaporated and the oily residue was chromatographed on silica gel (130 g), eluting with hexane/chloroform (1/4), and the products were crystallized from chloroform. 2,2,3-tribromo-2,3-dihydro-3-methylinden-1-one (**14**) 395 mg, 30% colorless crystals, mp 150-152 °C, (Found: C 31.39, H 1.85, C₁₀H₇Br₃O₂, requires C 31.37, H 1.84%), MS *m/z* 292, 290, 288 (M⁺, -Br), 211, 209, 207 (M⁺, -Br), 131,130 (M⁺, -Br), 103, 102, 101 (M⁺, -CO) IR (KBr, cm⁻¹) 1765 (-C=O)

2-bromo-3-(bromomethyl)1H-inden-1-one (**15**) 813 mg, 62% orange crystals, mp 156-158 °C, (Found: C C₁₀H₆Br₂O requires C 39.77, H 2.00%), MS *m/z* 303, 301, 299 (M⁺, -Br), 223, 222, 221, 220 (M⁺, -CO), 194,193 (M⁺, -Br), IR (KBr, cm⁻¹) 1717 (-C=O)

Photobromination of 4-nitro indane (16)

A solution of bromine (12.3 mmol, 1.96 g) in CCl₄ (10 mL) was added dropwise over 30 min to a stirred solution of 4-nitroindane (**16**) (500 mg, 3.06 mmol) in CCl₄ (60) in a photochemical reaction apparatus with irradiation by 150 W projector lamp. After completion of the reaction (60 min), the excess of bromine and the

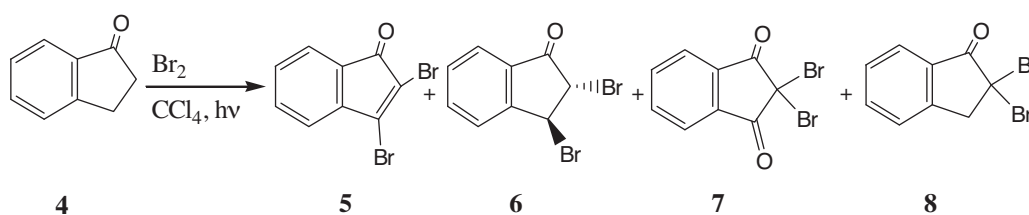
solvent were removed at reduced pressure at 35 °C. The dark residue was crystallized from chloroform to give 1,1,3-tribromo-4-nitro indane (**17**).

1,1,3-tribromo-4-nitro-indan (**17**) 1.1 g, 90% colorless crystals, mp 208-210 °C, (Found: C 27.95, H 1.15 C₁₀H₇BrO₂ requires C 27.03, H 1.51, MS *m/z*, 401 (M⁺, -NO₂), 355,353, 351 (M⁺, -2 Br), 195, 193 (M⁺, -Br), IR (KBr, cm⁻¹) 1529 (-NO₂).

Results and discussion

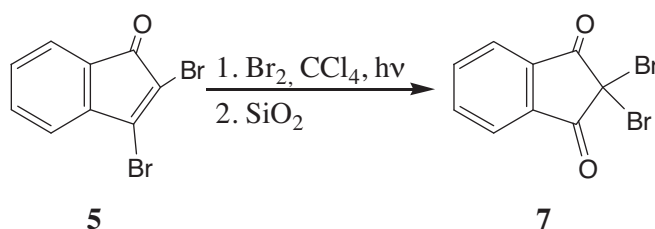
We focused on the bromination of 1-indanone (**4**), 2-methyl-1-indanone (**9**), 3-methyl-1-indanone (**13**), and 4-nitro indan (**16**). Benzylic bromination requires either a high temperature⁵ or irradiation with uv light,¹⁶ and often gives mixtures of products. In the bromination reactions, bromine (4 equiv.) was added to a solution of **4**, **9**, **13**, **16**, or **18**, in CCl₄ with internal irradiation (150 W projector lamp) at room temperature.

The ¹H-NMR studies revealed that the reaction mixture was very complex and consisted of 4 products formed after 60 min of irradiation in the photobromination of 1-indanone (**4**) (Scheme 2). The reaction mixture was crystallized from chloroform and dibromo indanone **8** was isolated in a yield of 15%. The methylene protons (H₃) and C₃-carbon in ¹H-NMR and APT spectra confirm the structure of dibromo indanone **8**. The rest was subjected to repeated column chromatography and 3 additional products, dibromo indenone **5**¹⁶, *trans*-dibromid **6**,^{26,27} and dibromo indandione **7**²⁸ were isolated, in yields of 39%, 10%, and 18%, respectively. The structures were established easily from ¹H-NMR and ¹³C-NMR spectra. The main isolated product, 2,3-dibromo indenone **5**¹⁶, was already characterized.¹⁶ Four aromatic protons in the ¹H-NMR spectrum and 9 signals in the ¹³C-NMR spectrum of dibromo indenone **5** were in complete agreement with the proposed structure. The ¹H-NMR spectrum of *trans*-dibromide **6**,^{26,27} which shows absorption at 4.27 (d, H₂, *J*_{2,3} = 2.2 Hz) and 5.99 (d, H₃), is in good agreement with the literature. The ¹H-NMR and ¹³C-NMR spectra of dibromo indandion **7** were highly symmetrical owing to the symmetry in the molecule.



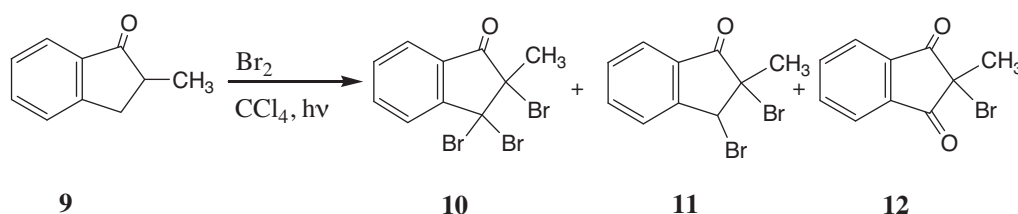
Scheme 2

We assume that this dibromo indandion **7**²⁸ is formed after further bromination of initially formed dibromo indenone **5**. In order to verify this finding, dibromo indenone **5** was submitted to further photobromination, which resulted exclusively in the formation of dibromo indandione **7** in 95% yield (Scheme 3). We assume that dibromo indandion **7** gave a hydrolysis reaction with the silica gel used in column chromatography.



Scheme 3

After the successful synthesis and isolation of polybrominated indan-1-one and inden-1-one derivatives, we were interested in the photobromination of 2-methyl indanone (**9**) (Scheme 4). Bromination of 2-methyl indanone with 4 equiv. of bromine afforded 3 products, which were characterized as tribromo indanone **10**, dibromo indanone **11**, and monobromo indandione **12** in yields of 53%, 20%, and 20%, respectively, and which were easily separated by column chromatography.



Scheme 4

Four aromatic signals and 1 methyl signal at 2.33 ppm were observed in the $^1\text{H-NMR}$ spectrum of tribromo indanone **10**. The proton signals adjacent to the bromine appear as a singlet at 5.95 ppm and methyl protons appear as a singlet at 2.10 ppm in the $^1\text{H-NMR}$ spectrum of dibromo indanone **11**. The 10 signals in the $^{13}\text{C-NMR}$ spectrum are also in agreement with the proposed structure. The $^1\text{H-NMR}$ spectrum of monobromo indandione **12** shows 1 aliphatic signal as a singlet at 1.25 ppm.

The addition of bromine to 3-methyl indanone (**13**) in carbon tetrachloride was found to give 2 products, 2,2,3-tribromo-2,3-dihydro-3-methylinden-1-one (**14**) and 2-bromo-3-bromomethyl-1H-inden-1-one (**15**) (Scheme 5). The reaction was carried out under nitrogen atmosphere and it was seen that dibromo indanone yielded only 1 product, dibromo indenone **15**. These results indicate that the air oxygen inserts into the carbon-carbon bond in the dibromo indanone **14**. The $^1\text{H-NMR}$ spectrum of **14** shows 1 aliphatic signal as a singlet at 4.27 ppm. Four aromatic signals and 1 methylene signal at 4.39 ppm were observed in the $^1\text{H-NMR}$ spectrum of dibromo indenone **15**. Elemental analysis and $^{13}\text{C-DEPT}$ spectrum of dibromo indenone **15** are in agreement with the proposed structure.

In addition, we were interested in the photobromination of 2,3-dihydro-4-nitro-1H-indene (**16**) (Scheme 6). Addition of bromine to 2,3-dihydro-4-nitro-1H-indene (**16**) gave only 1 product, which was characterized as 1,1,3-tribromo-2,3-dihydro-4-nitro-1H-indene (**17**) with 90% yield. $^1\text{H-NMR}$ absorptions observed at 8.2-7.6 ppm (3 aromatic signals), 6.1 ppm (dd, H_3 , $J_{3,2a}=5.5$, $J_{3,2b}=2.6$ Hz), 3.81 ppm (d, H_{2a}), and 3.79 ppm (d, H_{2b}), as well as the 9 signals in the $^{13}\text{C-NMR}$ spectrum, are also in agreement with the proposed structure (Table).

Table. NMR spectral data of some substituted indan derivatives

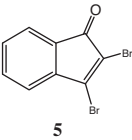
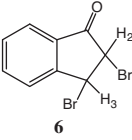
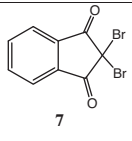
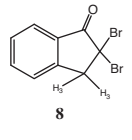
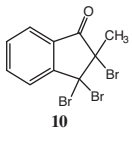
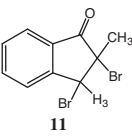
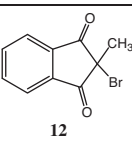
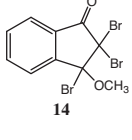
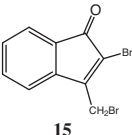
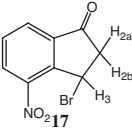
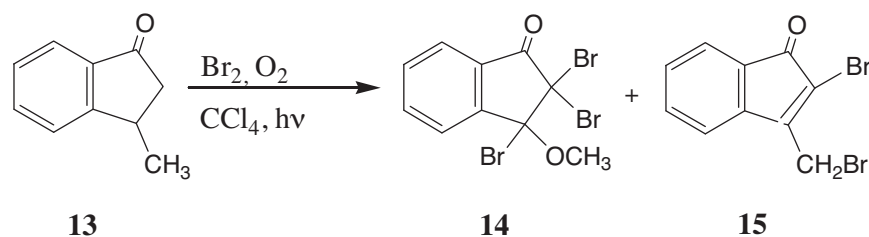
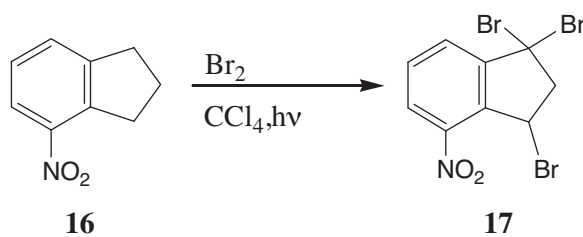
Compound	¹ H-NMR Resonances in ppm					Coupling Constant <i>J</i> (Hz)	¹³ C-NMR
	H ₁	H ₂	H ₃	Subs.	Aromatic		
 5	-	-	-	-	AB d, 7.08, t, 7.23 t, 7.33, d, 7.37	<i>J</i> _{aro.} =7.3	186.8, 146.6, 142.8, 134.6, 130.1, 129.3, 123.2, 122.6, 121.3
 6	-	d 4.27	d 5.99	-	AB d, 7.81, t, 7.74, d, 7.72, t, 7.52	<i>J</i> _{aro.} =7.7 <i>J</i> _{2,3} =2.2	186.5, 142.7, 137.3, 131.1, 129.3, 127.3, 126.3, 58.1, 52.6
 7	-	-	-	-	AA'BB' 8.1-8.01		87.4, 138.1, 135.9, 125.9, 51.5
 8			s 4.28		AB d, 7.93, t, 7.72 t, 7.49, d, 7.4	<i>J</i> _{aro.} =7.7	192.3, 147.3, 137.1, 137.1, 129.2, 126.8, 126.2, 57.1, 52.6
 10	-	-	-	s 2.33	AB d, 7.88, t, 7.77, d, 7.75, t, 7.54	<i>J</i> _{aro.} =7.7	191.5, 153.1, 136.2, 131.5, 129.8, 125.8, 125.3, 72.5, 64.6, 24.2
 11	-	-	s 2.01	s 5.95	AB d, 7.81, t, 7.70, d, 7.62, t, 7.51	<i>J</i> _{aro.} =7.7	196.4, 150.1, 136.5, 131.8, 130.7, 127.5, 125.8, 61.5, 55.2, 26.1
 12	-	-	-	s 1.53	AA'BB' 8.05-7.91		199.9, 139.8, 136.9, 124.5, 29.9, 22.3
 14	-	-	-	s 4.27	AB d, 7.91, t, 7.71, t, 7.48, d, 7.40	<i>J</i> _{aro.} =7.7	192.9, 147.3, 137.2, 129.2, 129.2, 126.8, 126.3, 57.1, 52.6, 52.6

Table. Continued.

Compound	¹ H-NMR Resonances in ppm					Coupling Constant <i>J</i> (Hz)	¹³ C-NMR
	H ₁	H ₂	H ₃	Subs.	Aromatic		
 15	-	-	-	s 4.39	AB d, 7.51, t, 7.44, d and t, 7.27	<i>J</i> _{aro.} =7.7	189.2, 153.9, 142.6, 134.7, 129.6, 129.4, 124.1, 121.1, 120.3, 21.8
 17	-	d, d 3.81, 3.79	d (H _{3a}) 6.10 d (H _{3b}) 6.08	-	d, 8.24, d, 8.09 t, 7.71	<i>J</i> _{3,2a} = 5.5, <i>J</i> _{3,2b} = 2.6, <i>J</i> _{5,6} = <i>J</i> _{6,7} =8.1	150.4, 143.7, 134.3, 132.2, 132.1, 126.9, 60.2, 53.4, 43.8



Scheme 5



Scheme 6

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