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Photobromination of indane: preparation of bromoindenones and ready access to benzo[*c*]fluorenone skeleton

Ahmet Tutar,[a,b] Osman Cakmak[a,*] and Metin Balci[b,*]

[a]*Department of Chemistry, Faculty of Science, Gaziosmanpasa University, 60240 Tokat, Turkey*
[b]*Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey*

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Abstract—1,1,3,3-Tetrabromoindane and 1,1,2,3,3-pentabromoindane were efficiently synthesized by photolytic bromination of indane. Subsequent dehydrobromination of them gave the corresponding tribromo- and tetrabromoindenes, which were easily converted to the corresponding bromoindenones by silver-supported hydrolysis. Thermolysis of 3-bromoindenone gave the benzo[*c*]fluorenone derivative.

1. Introduction

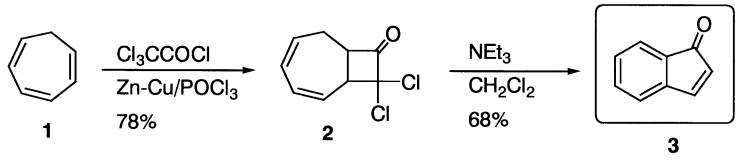
A rapid growth on the synthetic work of indenones has taken place in the last three decades. Indenones are useful intermediates[1] in the synthesis of a variety of molecules, including the C-nor D-homosteroid ring system,[2] photochromic indenone oxides,[3] 2,4- and 3,4-disubstituted-1-naphtols,[4] gibberellins,[5] indanones[6] and indenes.[7]

A logical precursor to these compounds could be the corresponding indenone. However, poor yields, irreproducibility, or decomposition of the starting material were common outcomes. Despite the considerable biological and synthetic interest in indenones, the development of general and flexible synthetic routes to these compounds still remains a challenging problem. Several procedures for the synthesis of indenones and indenols have been reported.[8] Mainly, two methods have been directed towards the synthesis of indenone derivatives. The first one[1,9] is the palladium or aluminium chloride catalyzed addition of substituted benzoyl chlorides to acetylenic compounds. The second method[10,11] involves an intramolecular Friedel–Crafts acylation of β-chloro-β-arylpropionyl chlorides followed by a dihydrochlorination reaction. In a previous paper, we reported the facile formation of indenone (**3**) by treatment of the product **2** formed from the addition of dichloroketene to cycloheptatriene (**1**), with base (Scheme 1).[12]

In this paper, we describe a new method leading to the synthesis of brominated indenone derivatives which can serve as the key compounds for the preparation of other substituted indenone derivatives as well as for construction of the benzo[*c*]fluorenone skeleton.

2. Results and discussion

First, we focused on the development of a practical process for the synthesis of 1,1,3,3-tetrabromoindane starting from indane. Bromination of hydrocarbons is important process because it leads to useful intermediates for the synthesis of a large variety of bromoorganic compounds. Benzylic bromination requires either high temperature or irradiation with UV light in the presence of free radical catalysts and often gives mixtures of products. Recently, we realized that internal irradiation of tetraline in the presence of bromine



Scheme 1.

Keywords: photobromination; bromoindenes; bromoindenones; benzo[*c*]fluorene.
* Corresponding authors. Tel.: +90-312-210-5140; fax: +90-312-210-1280; e-mail: ocakmak@gop.edu.tr; mbalci@metu.edu.tr

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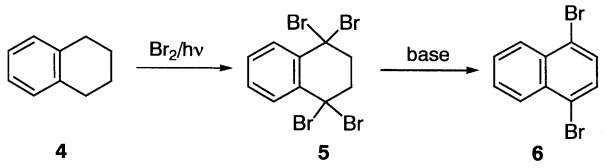


Scheme 2.

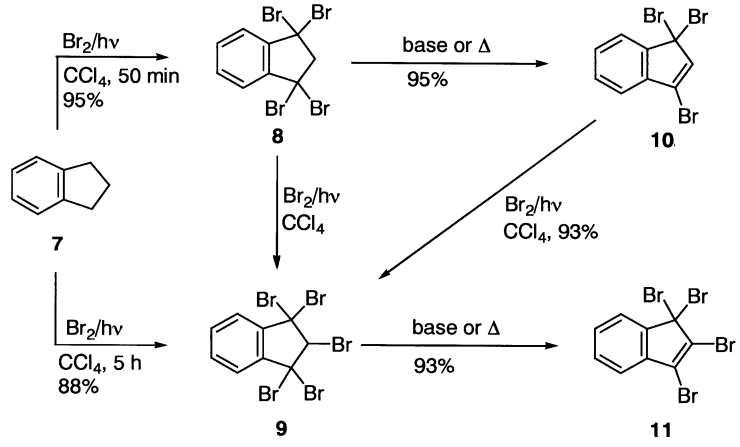
provides effective benzylic bromination and gives α,α,α′,α′-tetrabromotetraline **5** in high yield (Scheme 2).[13]

We describe herein the preparation of α,α,α′,α′-tetrabromoindane and the conversion of the photoproducts. To a solution of indane (**7**) in CCl_4 was added 4 equiv. bromine while internal irradiating (150 W projector lamp) at room temperature. The tetrabromide **8** was formed as the sole product in high yield (95%) after 50 min irradiation. The structure was established easily from the simple ^1H NMR spectrum consisting of a AA′BB′ system in the aromatic region and a singlet at 4.4 ppm arising from the methylenic protons. However, prolonged irradiation of **7** resulted in the formation of the pentabromide **9** (Scheme 3). Furthermore, the pentabromide **9** was obtained independently by irradiation of **10** in the presence of bromine.

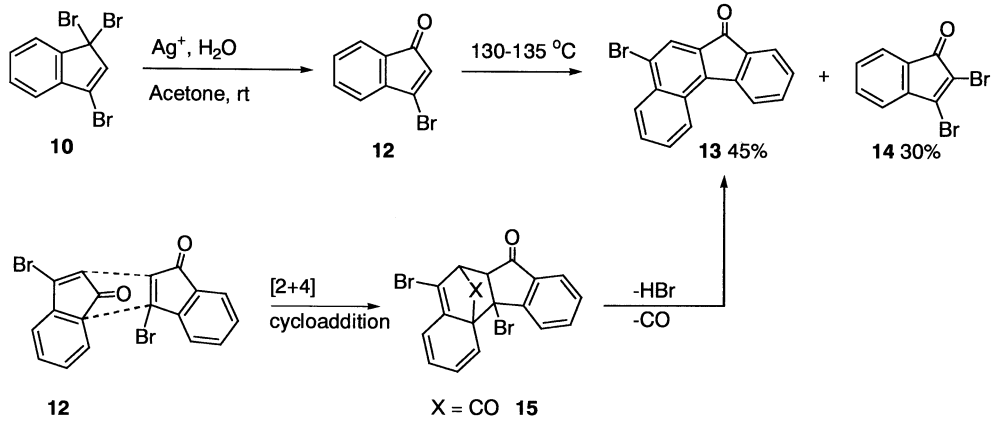
After successful synthesis and isolation of polybrominated indane derivatives **8** and **9**, which have the requisite arrangement and functionality to permit the easy introduction of one double bond to give bromoindenes, we submitted these compounds to a dehydrobromination reaction with 1 mol of potassium *tert*-butoxide or thermal decomposition without solvent at elevated temperatures (140–150°C) and isolated **10** and **11** in high yields, respectively (Scheme 3). The first synthesis of tribromoindene **10** was reported by Straus et al.[14] According to this procedure, indene gave the tribromide **10** in 68% yield upon treatment with KOBr solution. Later, Proctor[15] has observed the formation of tribromide **10** as a mixture with 1,2,3-tribromoindene by the bromination of indane with *N*-bromosuccinimide in the presence of light.

gem-Dibromides **8**–**11** are also precursors to the corresponding ketones. Therefore, the bromides were subjected to a silver ion-supported hydrolysis reaction in aqueous acetone. Tribromoindene **10** afforded bromoindenone **12**[16] in 90% yield (Scheme 4).

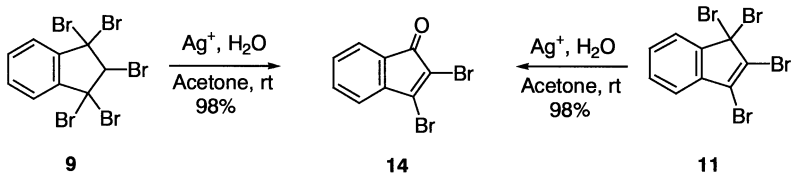
Next, we were interested in the thermal stability of the bromoindenone **12** derivative, since this compound contains an antiaromatic cyclopentadienone structure. When bromoindenone **12** was heated in a sealed tube in the absence of solvent, two separable products were isolated. Spectroscopic studies indicated the formation of **13** and **14** in 45 and 30% yields, respectively. The compound **13**[17] bearing a benzofluorenone structure was characterized by



Scheme 3.



Scheme 4.



9 14 11

Scheme 5.

means of ^{1}H and ^{13}C NMR spectroscopic data and two-dimensional spectral measurements (COSY, HMQC and HMBC). For the formation of this benzofluorenone structure, we suggest the following mechanism. Bromoindenone **12** undergoes an intramolecular [2+4] cycloaddition reaction where the cyclopentadienone structure acts as both the diene and the dienophile as depicted in Scheme 4. The formed intermediate **15** can easily undergo HBr elimination followed by CO extrusion to give 5-bromo-7*H*-benzo[*c*]fluoren-7-one **13**. The isolated by-product, 2,3-dibromoindenone **14** was characterized properly. However, its mechanism of formation is unclear.

For further characterization of **14**, we have undertaken an independent synthesis of **14** starting from pentabromoindane and tetrabromoindene derivatives **9** and **11**. Silver ion supported solvolysis of **9** and **11** in aqueous acetone solution resulted in the formation of the dibromoindenone **14** in 98% yield in both cases (Scheme 5).

3. Conclusion

A short and convenient method for the synthesis of highly brominated indane derivatives has been developed starting from indane. The reactions described in this paper appear to be fairly general and provide a useful method for introducing bromine atoms into benzylic positions. Upon treatment of the highly brominated indane derivatives with silver salt in aqueous acetone, the corresponding ketones were synthesized in high yield. Bromoindenone **12** was converted into the benzofluorenone derivative **13**. To the best of our knowledge, this is the shortest synthesis of this skeleton bearing a functional group, which can be easily replaced by other functional groups.

4. Experimental

4.1. General

Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Thin layer chromatography was carried out on Merck silica F_{254} 0.255 mm plates. Classical column chromatography was performed using Merck 60 (70–230 Mesh) silica. Melting points were determined on a Thomas–Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. IR spectra were recorded on an Jasco FT-IR 430. NMR spectra were recorded on a Bruker instrument 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR.

4.2. General procedure for photobromination

All bromination reactions were carried out in a cylindrical vessel with two necks attaching to a dimrot cooler and dropping funnel. For the internal irradiation, a 150 W projector lamp was used.

4.2.1. Photochemical bromination of indane (7). A solution of bromine (8.00 g, 50 mmol) in carbon tetrachloride (20 mL) was added to a magnetically stirred solution of indane (1.44 g, 12.2 mmol) in CCl_4 (35 mL) in a photochemical reaction apparatus (60 mL) dropwise over 35 min while irradiating by 150 W projector lamp. HBr was rigorously evacuated during the reaction. After completion of the reaction (50 min), the excess bromine and solvent were removed at reduced pressure and at 20°C, the solid residue was crystallized from chloroform at room temperature during two days to give colorless cubic crystals of *1,1,3,3-tetrabromoindane* (**8**) (5.0 g, 95%. Decomp.: 147–150°C; [Found: C, 24.79; H, 1.32. $C_9H_{10}Br_4$ requires C, 24.92; H, 1.39%]; ν_{max} (KBr) 2940, 1460, 1283, 1233, 1009, 865, 761, 600, 540 cm^{-1}; δ_H (400 MHz, $CDCl_3$) δ 7.7–7.5 (AA′BB′, 4H, aryl), 4.4 (s, 2H, methylenic); δ_C (100 MHz, $CDCl_3$) 142.8, 131.7, 125.0, 73.2, 51.8; MS (*m/z*): 430/432/434/436/438 (M^+), 349/351/353/355 (M^+, −Br), 271/273/275 (M^+, −2Br, 192/194 (M^+, −3Br) 113 (M^+, −4Br).

4.2.2. Synthesis of 1,1,2,3,3-pentabromoindane (9). A solution of bromine (7.61 g, 47.6 mmol) in carbon tetrachloride (20 mL) was added to a magnetically stirred solution of indane (**7**) (1.11 g, 9.4 mmol) in 35 mL CCl_4 and irradiated as described above for 4 h. After evaporation of the unreacted bromine and solvent at reduced pressure and 20°C, the solid residue was recrystallized from methylene chloride–hexane to give **9** (4.51 g, 88%). Decomp.: 140°C (colorless crystals); [Found: C, 21.10; H, 0.92. $C_9H_5Br_5$ requires C, 21.09; H, 0.98%]; ν_{max} (KBr) 2934, 1460, 1252, 1198, 1178, 1024, 880, 812, 760, 599, 528 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.7–7.5 (AA′BB′ 4H, aryl), 5.3 (s, 1H, methine); δ_C (100 MHz, $CDCl_3$) δ 140.7, 132.1, 125.7, 75.9, 58.3; MS *m/z* 512/514 (M^+), 429/431/433/435/437 (M^+, −Br, 25), 351/353/355/357 (M^+, −2Br, 11), 271/273/275 (M^+, −3Br, 75), 191/193 (M^+, −4Br, 11), 113 (M^+, −5Br, 100).

4.2.3. Synthesis of 1,1,3-tribromo-1*H*-indene (10). *(a) Thermal reaction of tetrabromide* **8**. A crystalline material of **8** (1.39 g, 3.21 mmol) in a sealed glass-tube was allowed to heat in silicon oil bath to 150–155°C for 30 min. The elimination of HBr was observed. The dark-colored material was filtered through a short column (10 g alumina) eluting with hexane. The solvent was evaporated. The residue was crystallized from hexane–ether (1:2, 9 mL) in a freezer to

give colorless crystals, mp: 106°C (Lit. mp: 104.5–105°C) (1.07 mg, 95%).

(b) Elimination of tetrabromide **8** *with potassium tert-butoxide*. To a stirred solution of tetrabromide **8** (2.5 g, 5.8 mmol) in dry and freshly distilled THF (70 mL) was added potassium *tert*-butoxide (0.76 g, 6.8 mmol). The resulting reaction mixture was stirred 12 h at room temperature. The mixture was diluted with water (40 mL), the aqueous solution was extracted with ether (60 mL), washed with water (40×2 mL), and dried over $MgSO_4$. After removal of the solvent, the residue (pale-yellow oil) was filtered on a short silica gel column (15 g) eluted with hexane. The product was crystallized (hexane–diethyl ether: 1:2, 6 mL) to give pure **10** (1.67 g, 82%); [Found: C, 30.60; H, 1.35. $C_9H_5Br_3$ requires C, 30.64; H, 1.43%]; ν_{max} (KBr) 3114, 1544, 1258, 1202, 951, 864, 780, 750, 704, 683, 647 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.7 (m, 1H), 7.4 (m, 2H), 7.3 (m, 1H), 6.85 (s, olefinic); δ_C (100 MHz, $CDCl_3$) 147.0, 139.8, 135.2, 130.0, 129.2, 124.1, 122.4, 121.1, 50.8; MS *m/z* 350/352/354/356 (M^+), 271/273/275 (M^+, −Br, 35), 192/194 (M^+, −2Br, 15), 113 (M^+, −3Br, 100).

4.2.4. Synthesis of 1,1,2,3-tetrabromo-1*H*-indene (11). *(a) Thermal dehydrobromination of pentabromide* **9**. Pentabromide **9** (1.51 g, 3.4 mmol) in a sealed glass-tube was allowed to heat in silicon oil bath to 120°C for 30 min. The dark-colored material was filtered through a short Al_2O_3 (15 g) column eluted with hexane. After evaporation of the solvent, the residue was crystallized from CH_2Cl_2–hexane (1:3, 10 mL) at room temperature to give tetrabromoindene **11**, mp 124°C (1.18 g, 93%).

(b) Base-induced elimination reaction of pentabromide **9**. To a stirred solution of pentabromide **9** (2.60 g, 5.1 mmol) in dry and freshly distilled THF (50 mL) was added (0.66 g, 5.9 mmol) potassium *tert*-butoxide. The resulting reaction mixture was stirred 12 h at room temperature. The mixture was diluted with water (30 mL), and the aqueous solution was extracted with ether (50 mL), washed with water (30×2 mL), and dried over $MgSO_4$. After removal of the solvent, the oily residue was filtered on a short silica gel column (10 g) eluted with hexane to give **11** (1.71 g, 78%); [Found: C, 24.96; H, 0.90. $C_9H_8Br_4$ requires C, 25.04; H, 0.93%]; ν_{max} (KBr) 3048, 1460, 1238, 1171, 1118, 890, 770, 753, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.7 (brd, 1H), 7.4 (m, 2H), 7.3 (m, 1H); δ_C (100 MHz, $CDCl_3$) 145.9, 135.0, 133.9, 130.3, 129.1 124.8, 124.2, 120.8; 54.74; MS *m/z* 428/430/432/434/436 (M^+), 349/351/353/355 (M^+, −Br, 25), 272/274/276 (M^+, −2Br), 191/193 (M^+, −3Br, 100), 113 (M^+, −4Br, 71).

4.2.5. Photobromination of 1,1,3-tribromo-1*H*-indene (10). To a solution of **10** (120 mg 0.34 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube was added bromine (66 mg, 0.41 mmol). The mixture was irradiated by a projector lamp (150 W) for 10 min. The residue obtained after removal of the solvent was crystallized from CH_2Cl_2–petroleum ether to give 1,1,2,3,3-pentabromoindane **9** (162 mg, 93%).

4.2.6. Synthesis of 3-bromo-1*H*-inden-1-one (12). A solution of $AgClO_4$ (3.60 g, 17.16 mmol) in aqueous acetone (25 mL acetone/5 mL H_2O) was added to a stirred solution of 1,1,3-tribromo-1*H*-indene (**10**) (2.75 g, 7.80 mmol) in acetone (50 mL) over 5 min. The resulting mixture was stirred magnetically at room temperature for 30 min. The precipitated silver bromide was removed by filtration. 50 mL methylene chloride was added to organic phase and washed with H_2O (3×40 mL), and dried over $MgSO_4$. The solution was concentrated under reduced pressure. Complete removing of the solvent should be avoided, since the product decomposes. However, it is stable after crystallization. Crystallization from CH_2Cl_2–petroleum ether (1:1, 10 mL) in a refrigerator yielded 3-bromoindenone **12** (1.47 g, 90%) as yellow needles, mp 57°C, (Lit mp 57.5–58°C[16]). ν_{max} (KBr) 1716, 1538, 1365, 1245, 1075, 912, 762, 683, 599, 554, 413 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39 (dt, *J*=7.5, 1.1 Hz, 1H), 7.34 (brd, *J*=7.0 Hz, 1H), 7.26 (brt, *J*=7.2 Hz, 1H) 7.12 (brd, *J*=7.3 Hz, 1H), 6.14 (s, 1H, olefinic); δ_C (100 MHz, $CDCl_3$) 193.8, 148.6, 142.9, 133.6, 130.4, 127.34, 121.8, 121.3.

4.2.7. Synthesis of 2,3-dibromo-1*H*-inden-1-one (14). *(a) Silver ion-promoted hydrolysis of pentabromoindane* **9**. A solution of $AgClO_4$ (5.55 g, 26.75 mmol) in aqueous acetone (40 mL acetone/10 mL H_2O) was added to a stirred solution of 1,1,2,3,3-pentabromoindane (**9**) (3.15 g, 6.14 mmol) in acetone (100 mL) over 5 min. The resulting mixture was stirred at room temperature for 30 min. The precipitated AgBr was removed by filtration. To the organic phase was added methylene chloride (60 mL) and organic phase was washed with water (30×2 mL) and dried over Na_2SO_4. After removal of the solvent, the residue was crystallized from methylene chloride–hexane (1:1, 25 mL) by standing in refrigerator to give 2,3-dibromo-1*H*-inden-1-one (**14**), yellow needless, (1.75 g, 98%). mp 120°C. (Lit. mp 123°C[17]).

(b) Silver ion-promoted hydrolysis of 1,1,2,3-tetrabromo-1H-indene **11**. A solution of $AgClO_4$ (1.27 g, 6.2 mmol) in aqueous acetone (25 mL acetone/5 mL H_2O) was added to a solution of 1,2,3,3-tetrabromoindene (**11**) (1.30 g, 3.0 mmol) in acetone (100 mL) over 10 min. After stirring at room temperature for 30 min, the precipitated AgBr was removed by filtration. To the filtrate was added methylene chloride (70 mL) and organic layer was washed with water (40×2 mL) and dried over Na_2SO_4. After removal of the solvent, the residue was crystallized from methylene chloride–hexane (1:1, 25 mL) by standing in refrigerator to give **14** (98%); [Found: C, 37.81; H, 1.45. $C_9H_4Br_2O$ requires C, 37.54; H, 1.40%]; ν_{max} (KBr) 1715, 1542, 1208, 1096, 752, 693, 657, 425 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39–7.35 (m, 2H), 7.45 (t, *J*=7.5 Hz, 1H), 7.12 (d, *J*=7.2, 1H); δ_C (100 MHz, $CDCl_3$) 186.5, 146.34, 142.5, 134.4, 129.9, 129.0, 122.9, 122.4, 121.1.

4.2.8. Thermal decomposition of 3-bromo-1*H*-inden-1-one (12). Bromoindenone **12** (0.44 g) was heated in a sealed glass-tube at 130–135°C for 5 h. The dark residue was subjected to silica gel chromatography (40 g) eluting with hexane. The first fraction gave **14** 90 mg, 30%.

The second fraction was identified as *5-bromo-7H-benzo[c]fluoren-7-one* **(13)** (150 mg, 45%), mp 220°C (Lit. mp 220–221°C[17]) red crystals from methylene

chloride; [Found: C, 66.04; H, 2.45. $C_{17}H_9BrO$ requires C, 65.87; H, 2.52%]; ν_{max} (KBr) 1707, 1555, 1243, 880, 745, 694 cm^{-1}; δ_C (400 MHz, $CDCl_3$) 8.51 (dd, J=7.2, 1.6 Hz, 1H), 8.34 (dd, J=7.6, 1.5 Hz, 1H), 8.04 (s, 1H), 8.02 (d, J=7.6 Hz, 1H), 7.70 (m, 3H), 7.54 (t, J=7.6 Hz, 1H) 7.34 (t, J=7.4 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 193.5, 144.4, 142.2, 135.6, 134.7, 134.1, 131.9, 129.8, 129.6, 129.1, 129.0, 128.4, 125.2, 124.37, 124.33, 124.2, 123.5.

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