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## A CONVENIENT ONE-POT SYNTHESIS OF INDANE-1,2,3-TRIONES BY OXIDATION OF INDAN-1-ONES WITH N-BROMOSUCCINIMIDE-DIMETHYL SULFOXIDE REAGENT

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Abstract:Indane-1,2,3-triones  $(2_{a}-f)$  have been synthesized via bromination of indan-1-ones  $(1_{a}-f)$ , followed by oxidation of the resulting brominated indan-1-ones with dimethyl sulfoxide in one pot in good yields.

Vicinal polyketones are of increasing interest in photochemistry<sup>1</sup> and versatile intermediates in the synthesis of heterocyclic compounds,<sup>2</sup> highly substituted imidazoles,<sup>3</sup> and substituted furans.<sup>4</sup> Indane-1,2,3-triones and their monohydrates are of great importance in view of their wide application to analytical and synthetic purposes.<sup>5</sup> Thus, the oxidation of one or two methylene groups oriented at the vicinal position to a carbonyl group to give 1,2-di- or 1,2,3-trione has been recognized as a very important reaction in organic synthesis, and many procedures for the preparation of diones or triones have been developed.<sup>6</sup> Previously, we reported the one-pot synthesis of vicinal di-

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Scheme 1: Synthesis of Indane-1,2,3-triones from indan-1-ones by NBS-DMSO oxidation

and triketones via the corresponding sulfonium bromides from  $\alpha$  methylene carbonyl compounds by N-bromosuccinimide (NBS) dimethyl sulfoxide (DMSO) oxidation.<sup>7</sup>

When the reaction of indan-1-one with NBS in anhydrous DMSO was carried out at 80  $^{\circ}$ C under an ambient pressure, rapid decomposition of DMSO by the generated hydrogen bromide predominantly proceeded. Therefore, it was necessary in this oxidation reaction to prevent the acid-catalyzed decomposition of DMSO. In order to remove the generated hydrogen bromide, the oxidation reaction was carried out under reduced pressure with an aspirator. Thus, we have improved a convenient one-pot synthesis of indane-1,2,3-triones from indan-1-ones by NBS-DMSO oxidation (Scheme 1). We report herein this improved method for the preparation of the triones which were obtained in excellent yields.

A typical procedure is as follows: to a solution of 5-fluoroindan-1-one (1.50 g, 10.0 mmol) in anhydrous DMSO (40 ml), was added NBS (3.60 g, 20.2 mmol). The reaction mixture was heated at 40  $^{\circ}$ C for several hours. The progress of the reaction was monitored by TLC . After disappearance of the indan-1-one, the reaction mixture was further heated at 80  $^{\circ}$ C for 6 h under reduced pressure with an aspirator to remove the generated hydrogen bromide. It was then poured into water (200 ml), followed by extracting with dichloromethane (50 ml). The extract was washed with water and dried (MgSO<sub>4</sub>). After removal

Compds	$\mathbb{R}^1$	$\mathbb{R}^2$	R <sup>3</sup>	Mp (lit.) °C	Yield <sup>a</sup> %
2 <sub>a</sub>	Н	Н	H	252-254 (255) <sup>b</sup>	88
$2_{\rm b}$	Η	F	Н	98 - 99	75
2 c	Н	Cl	Н	65 - 67	86
$2{ m d}$	Η	Br	Н	184.5 - 185.5 (dec)	87
<b>2</b> e	Me	Н	Н	157 - 158	88
$2_{ m f}$	Η	Η	Me	148 - 149	82

Table 1 Physical Characters of Indane-1,2,3-triones, 2a - f

<sup>a</sup> isolated yield. <sup>b</sup> reference 9.

of the solvent the residue was chromatographed on  $SiO_2$  with dichloromethane as eluent. The first fraction collected was recrystallized from ethanol to give 0.37g (12%) of 2,2-dibromo-5fluoroindan-1-one.<sup>8</sup> One the other hand, the aqueous layer was saturated with brine and extracted with dichloromethane (4 x 100 ml). The combined organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo. The resulting residue was purified by column chromatography on  $SiO_2$  (dichloromethane) to afford 1.57 g (80%) of 5-fluoroninhydrin as a pale yellow needles. Table 1 summarizes the results obtained with several indane-1,2,3-triones.

Reasonable reaction pathway for this reaction is shown in Scheme 2. The initial step in the oxidation of indan-1-one (1a) is bromination to afford 3-bromoindan-1-one,<sup>10</sup> which is oxidized further to indane-1,3dione<sup>10</sup> by Kornblum oxidation with DMSO. The second step of the reaction pathway involves bromination of indane-1,3-dione. The resulting 2-bromoindane-1,3-dione reacts with DMSO to give the corresponding sulfonium bromide, which then yields indane-1,2,3-trione (**2a**).

In conclusion, the present reaction combines bromination of indan-1ones with NBS in DMSO and oxidation of the resulting brominated ketones with DMSO in one pot, which offers a general and convenient route for preparing indane-1,2,3-triones from commercially available indan-1-ones under mild conditions in good to excellent yields.



Scheme 2: Reaction pathway to indane-1,2,3-trione

### Experimental

Infrared spectra were recorded on Nihon Bunko 7300 FT-IR spectrometer in KBr with absorptions in cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on an Unity-plus-300 from a solution in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> of the product. <sup>1</sup>H chemical shifts are expressed as  $\delta$  values (ppm) relative to TMS as internal standard. Mass spectra were recorded on Hitachi 80-B spectrometer. Melting points (Mp) in  $\mathbb{C}$  are uncorrected. Commercial dimethyl sulfoxide was purified by drying over calcium hydride and distillation. Indan-1-ones (**1a** - **f**) were commercially available and were used without purification.

Indane-1,2,3-trione (2a): dark reddish-violet needles; IR(KBr) 1711(C=O), 1740(C=O), 1771(C=O) cm<sup>-1</sup>; MS (EI) m/z: 160 (M<sup>+</sup>, 20), 132 (53), 104 (100), 76 (90).

**5-Fluoroindane-1,2,3-trione** (2b): dark reddish-violet solids; IR(KBr) 1725(C=O), 1742(C=O), 1756(C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ, 7.32 - 8.14(m, 3H, ArH); <sup>13</sup>C NMR(DMSO-d<sub>6</sub>): δ, 111.49(J=22.7 Hz), 125.48(J=23.9Hz), 128.96(J=9.8Hz), 138.30(J=2.9Hz), 144.03(J=9.2Hz), 167.33(J=258.6Hz), 183.96, 183.30, 186.51; MS (EI) m/z: 178 (M<sup>+</sup>, 20), 150 (74), 123 (98), 94 (100). HRMS calcd for C<sub>9</sub>H<sub>3</sub>FO<sub>3</sub> [M<sup>+</sup>] 178.0066, found 178.0071.

#### **INDANE-1,2,3-TRIONES**

**5-Chloroindane-1,2,3-trione (2c):** dark reddish-violet needles; IR(KBr) 1731(C=O), 1752(C=O), 1763(C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$ , 7.87(dd, J=8.3, 2.0Hz, 1H, ArH), 7.99(d, J=8.3Hz, 1H, ArH), 8.00(d, J=2.0Hz, 1H, ArH); <sup>13</sup>C NMR(DMSO-d<sub>6</sub>):  $\delta$ , 124.72, 127.30, 137.59, 138.89, 142.88, 144.07, 183.53, 183.76, 186.28; MS (EI) m/z: 194, 196 (M<sup>+</sup>, M<sup>+</sup> + 2, 6, 2), 166, 168 (25, 9), 138, 140 (100, 33), 109, 111 (70, 23). HRMS calcd for C<sub>9</sub>H<sub>3</sub>ClO<sub>3</sub> [M<sup>+</sup>] 193.9770, found 193.9807, [M<sup>+</sup> 2] 195.9740, found 195.9723.

**5-Bromoindane-1,2,3-trione (2d):** dark reddish-violet needles; IR(KBr) 1709(C=O), 1734(C=O), 1763(C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$ , 7.90(d, J=8.4Hz, 1H, ArH), 8.18(s, 1H, ArH), 8.19(d, J=8.4Hz, 1H, ArH); <sup>13</sup>C NMR(DMSO-d<sub>6</sub>):  $\delta$ , 127.27, 127.74, 131.64, 139.74, 141.05, 143.18, 183.40, 184.02, 186.31; MS (EI) m/z: 238, 240 (M<sup>+</sup>, M<sup>+</sup> + 2, 8, 7), 210, 212 (31, 26), 182, 184 (97, 100). HRMS calcd for C<sub>9</sub>H<sub>3</sub>BrO<sub>3</sub> [M<sup>+</sup>] 237.9266, found 237.9270, [M<sup>+</sup> 2] 239.9245, found 239.9238.

**5-Methylindane-1,2,3-trione (2e):** dark reddish-violet solids; IR(KBr) 1722(C=O), 1752(C=O), 1784(C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$ , 2.77(s, 3H, Me), 7.43 - 7.95(m, 3H, ArH); <sup>13</sup>C NMR(DMSO-d<sub>6</sub>):  $\delta$ , 23.00, 124.94, 125.05, 138.74, 139.55, 141.67, 149.91, 184.54, 185.01, 186.87; MS (EI) m/z: 174 (M<sup>+</sup>, 13), 146 (71), 118 (100), 89 (98). HRMS calcd for C<sub>10</sub>H<sub>6</sub>O<sub>3</sub> [M<sup>+</sup>] 174.0317, found 174.0322.

**4-Methylindane-1,2,3-trione (2f):** dark reddish-violet solids; IR(KBr) 1722(C=O), 1752(C=O), 1782(C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ, 2.74(s, 3H, Me), 7.38 - 7.91(m, 3H, ArH); <sup>13</sup>C NMR(DMSO-d<sub>6</sub>): δ, 19.54, 122.60, 137.17, 137.70, 139.44, 139.77, 140.59, 184.96, 185.71, 188.39; MS (EI) m/z: 174 (M<sup>+</sup>, 7), 146 (67), 118 (93), 89 (100). HRMS calcd for C<sub>10</sub>H<sub>6</sub>O<sub>3</sub> [M<sup>+</sup>] 174.0316, found 174.0341.

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