

Anodically Promoted $2\pi + 2\pi$ Cycloaddition of Certain Indene Derivatives

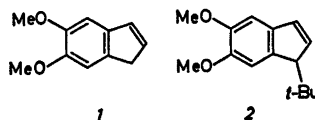
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The anodic oxidation of a dilute solution of 5,6-dimethoxyindene or 1-*t*-butyl-5,6-dimethoxyindene in acetic acid/potassium acetate results in the addition of two acetoxy groups across the double bond besides predominant polymer formation. No steric influence from the electrode surface on product composition was found. In concentrated solutions of these substrates the reaction takes an unexpected course, in that $2\pi + 2\pi$ cycloaddition dimers are formed in low yields, again with polymer formation predominant. The mechanism of the cycloaddition process is probably similar to that suggested for iron(III) salt catalyzed $2\pi + 2\pi$ cycloadditions.

The stereochemistry of the anodic addition of acetoxy groups to indene¹ and 1-alkylindenes² has been studied previously in order to elucidate possible effects of adsorption on the distribution of diastereomeric diacetates. During the course of this investigation Thompson and Naipawer showed by studies on another heterogeneous process, catalytic hydrogenation over a 5% Pd/C catalyst, that the methoxy substituent has a particularly strong adsorption-enhancing effect.³ Hence it became desirable to investigate the anodic oxidation of methoxy substituted indenenes, 5,6-dimethoxyindene (**1**) and 1-*t*-butyl-5,6-dimethoxyindene (**2**) being selected as representative substrates. This report shows that anodic addition of acetoxy groups is not a favored reaction with these compounds, but that they undergo an anodically promoted $2\pi + 2\pi$ cycloaddition under certain conditions.

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RESULTS

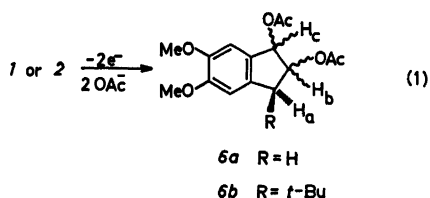
Synthesis of substrates 1 and 2. The synthesis of **1** has been described earlier.^{4,5} A somewhat modified procedure, *viz.* ring closure of 3-(3,4-dimethoxyphenyl) propanoic acid (**3**) in polyphosphoric acid followed by sodium borohydride reduction of 5,6-dimethoxy-1-indanone (**4**) and eventual elimination of water from 5,6-dimethoxy-1-indanol (**5**) was developed and gave **1** in an overall yield of 49% from **3**. It was found to be imperative that the work-up procedure for **5** did not involve any treatment with acid, since otherwise blue polymeric material was rapidly formed.

The synthesis of **2** was performed in essentially the same manner except that 3-*t*-butyl-5,6-dimethoxy-1-indanone was obtained in one step from veratrole and β -*t*-butylacrylic acid by polyphosphoric acid treatment⁷ and the final elimination step had to be carried out as a Chugaev reaction.⁶ In pyridine/acetic anhydride **2** rearranged to its isomer, 3-*t*-butyl-5,6-dimethoxyindene. The overall yield of purified **2** from veratrole was 34%.

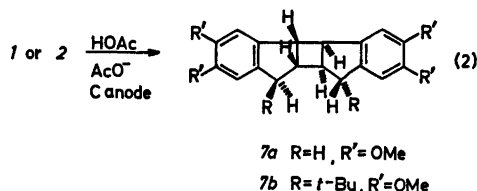
Anodic oxidation of 1 and 2. The introduction of the two 5,6-methoxy groups into the indene system lowered the half peak potential ($E_{p/2}$) by more than 500 mV.⁸ Thus, $E_{p/2}$ values for indene, 1-*t*-butylindene, **1**, and **2** were found to be 1.47, 1.39, 0.81, and 0.81 V *vs.* SCE,

respectively, in HOAc/KOAc (1 M) at the platinum anode. Preparative experiments with **1** and **2** were performed at 1.0 V vs. SCE.

Preparative anodic oxidation of **1** and **2** in HOAc/KOAc (1 M) at platinum or graphite electrodes gave polymeric material predominantly under all conditions tried. This made a detailed study of the stereochemistry of the addition reaction along the lines described earlier¹ impossible. From dilute solutions of **1** or **2** small amounts of diacetoxo products **6a** or **6b** (10 and 15 % yield, respectively) were indeed obtained (eqn. 1), but the low yields precluded any meaningful interpretation of the results.



From **1** at least two diacetates (**6a**) were detectable by GLC/MS but could not be isolated due to experimental difficulties. From **2** two diacetates in a ratio of 60:40 (**6b**) were isolated. They were assigned the *trans* arrangement of H_A and H_B (**6b**) by comparison of their ¹H NMR spectra with the corresponding isomers of 3-*t*-butyl-1,2-diacetoxoindan (60 % isomer: δ 3.07 (H_a), 5.64 (H_b), 6.26 (H_c), J_{ab} 2.0 and J_{bc} 5.4 Hz; 40 % isomer: δ 2.94 (H_a), 5.44 (H_b), 5.96 (H_c), J_{ab} 2.0 and J_{bc} 1.5 Hz; 3-*t*-butyl-1,2-diacetoxoindan: *cis* (ab) - *cis* (bc), δ 3.0 (H_a), 5.8 (H_b), 6.1 (H_c), J_{ab} 4.4 and J_{bc} 4.4 Hz; *cis* (ab) - *trans* (bc), δ 3.3 (H_a), 5.6 (H_b), 6.3 (H_c), J_{ab} 5.8 and J_{bc} 7.0 Hz; *trans* (ab) - *trans* (bc), δ 3.0 (H_a), 5.4 (H_b), 6.1 (H_c), J_{ab} 3.2 and J_{bc} 2.2 Hz; *trans* (ab) - *cis* (bc), δ 3.1 (H_a), 5.7 (H_b), 6.3 (H_c), J_{ab} 1.7 and J_{bc} 5.4 Hz).



The anodic oxidation of concentrated solutions of **1** and **2** in HOAc/KOAc gave an unex-

pected product, shown (see below) to be a cyclobutane derivative (**7**) formally resulting from a $2\pi + 2\pi$ cycloaddition reaction (eqn. 2). This product was isolated in 30 and 10 % yield from **1** and **2**, respectively.

The structural proof for **7** was based on the following evidence. Elemental analysis of **7a** and **7b** was the same as for the starting materials but their GLC retention times were considerably longer. The mass spectrum of **7a** at 70 eV had its 100 % peak at m/e 176 and the mass of the molecular ion at m/e 352 (0.1 %). At 11 eV the mass spectrum of **7a** had only two peaks, at m/e 176 (100 %) and 177 (12 %). This fragmentation pattern is characteristic for cyclobutane derivatives which are known to cleave predominantly according to a reverse cycloaddition mechanism.⁹ The mass spectral behavior of **7** was similar, the ion with m/e half that of the parent ion being the 100 % fragment at 70 eV.

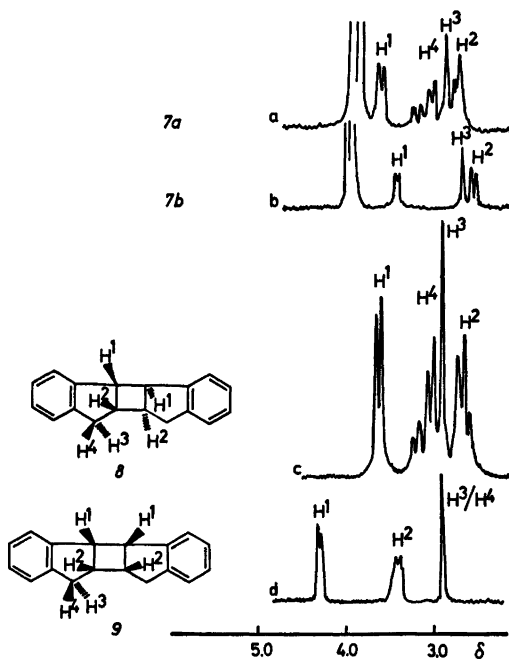


Fig. 1. ¹H NMR spectrum for the δ 2.4–4.6 region of **7a**, **7b**, **8**, and **9**. The remaining shifts are for **7a**: δ 3.92 and 3.88 (d, 6 H, CH₃O) and 6.78 and 6.88 (d, 2 H, Ar); for **7b**: δ 3.92 and 3.96 (d, 6H, CH₃O), 0.76 (d, 9 H, *t*-Bu), and 6.92 and 6.94 (d, 2 H, Ar). The spectrum of **9** was taken from Ref. 10.

The ^1H NMR spectra of $7a$ and $7b$ were compared with those of the known¹⁰ indene cyclodimers 8 and 9 (see Fig. 1). In selecting these compounds for comparison, we tacitly assumed that the dimerization process takes place *via* a radical cation mechanism similar to the iron(III) nitrate catalyzed $2\pi + 2\pi$ cycloaddition of *N*-vinylcarbazole.¹¹ For indene itself it is known¹ that the initial coupling between the radical cation and the parent compound takes place in a head-to-head fashion, thus limiting the possible types of cyclodimer structures to the one with methylene groups in the 1,2-position of the cyclobutane system. Thus, of the four possible cyclodimers of indene only 8 and 9 were of interest here.

Fig. 1 shows the region of δ 2.4–4.6 for these four compounds. The similarity between the spectra of $7a$ and 8 is striking, as indeed would be expected considering the small structural difference between them. The introduction of the methoxy groups would not be expected to have any significant effect on the shifts of the alicyclic hydrogens. In Fig. 1a couplings are seen between H^1 and H^2 , H^2 and H^4 , but not between H^2 and H^3 . Substitution of H^4 for a *t*-butyl group will give a spectrum with coupling between H^1 and H^2 , whereas H^3 will appear as a singlet (Fig. 1b). This is valid only if the steric arrangement around the cyclobutane ring is as shown for $7b$ in eqn. 2. The ^1H NMR spectrum of the other possible isomer (9) has the H^3 signal at a lower field than that of H^2 , contrarily to what is found for $7a$,

$7b$ and 8 . Taken together, structure $7b$ for the cyclodimer from 2 is strongly indicated from the ^1H NMR spectral studies.

Table 1 is a summary of ^{13}C NMR spectral data for $7a$, $7b$ and 8 . The influence of the methoxy groups upon the shifts of the alicyclic carbons is negligible. The appearance of the spectrum shows that the molecule must possess a C_2 axis as symmetry element.

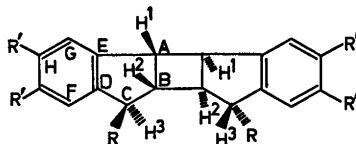
Several attempts to cyclodimerize 1 by treatment with iron(III) nitrate in acetic acid or methanol¹¹ were unsuccessful.

DISCUSSION

It was previously concluded² that the anode surface has no steric influence upon the anodic addition of acetoxy groups to 1-*t*-butylindene. The substitution of the 5,6-hydrogens for methoxy groups was made in order to see if the adsorption-enhancing properties of the methoxy group, strongly exhibited in catalytic hydrogenation, might drastically change the diastereomer distribution. Moreover, the lowering of the oxidation potential caused by the methoxy groups should help to bring the working anode potential closer to the potential of zero charge, at which maximum adsorption of neutral molecules takes place.¹²

It is, however, seen that there is no change in diastereomer distribution from the anodic addition of acetoxy groups to 1-*t*-butylindene² (62:38) or to 1-*t*-butyl-5,6-dimethoxyindene

Table 1. ^{13}C NMR chemical shifts for $7a$, $7b$, and 8 (δ , TMS).



Compound	A	B	C	D	E	F	G	H	J ^a	K ^b	L ^c
8	43.1	53.9	39.3	1146	144	125	125	127	55.		
$7a$	44.1	54.0	39.3	138	135	108	108	148	55.9		
$7b$	46.8	53.1	62.4 ^d	140	137	111	107	149 ^e	55.9	34.4	27.4

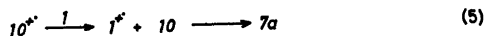
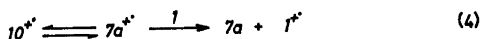
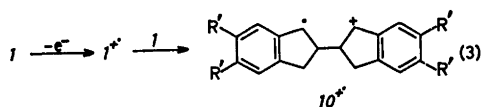
^a Methoxy carbons. ^b Quaternary *t*-butyl carbon. ^c Methyl carbons in *t*-butyl group. ^d A shift of 20 ppm is reasonable when H is substituted for *t*-butyl. ^e The other aromatic carbon 147.

(60:40). Thus the conclusion from the previous study² that no steric effect from the anode is indicated in this type of reactions is reinforced here.

The formation of cyclodimers from runs in concentrated solution is unexpected, since formally no electrochemistry need be involved in the overall formation of 7 from 1 or 2. A precedent for this type of process has been found earlier during the anodic oxidation of *N*-vinylcarbazole in acetonitrile¹³ which gave an 8% yield of 1,2-bis-(carbazol-9-yl)cyclobutane. No mechanism was suggested.

Certain metal ion catalysts, *e.g.* iron(III) nitrate, affect the same reaction with suitably substituted alkenes.¹¹ The mechanism was recently¹⁴ proposed to be a radical chain reaction, initiated by the formation of the radical cation in a 1-e transfer from the substrate to the metal ion. Also indene itself can be cyclodimerized by treatment with iron(III) chloride in acetonitrile,¹⁵ again assumed to take place *via* the radical cation.

The anodic cyclodimerization reaction reported here is most likely a radical chain reaction similar to that proposed for the iron(III) catalyzed reaction (exemplified by 1 in eqns. 3 and 4 or 3 and 5). In concentrated solutions the radical cation is preferentially trapped by 1, whereas in dilute solution reaction with acetate ion will predominate.



EXPERIMENTAL

All controlled potential electrolyses were carried out in waterjacketed cells of either 30 or 150 cm³ volume. For electrodes, see Ref. 2. The potential was kept at 1.0 V *vs.* SCE by a

potentiostat, built by the Electronics Service Division of this Department.

3-(3,4-Dimethoxyphenyl)propanoic acid. A solution of 3,4-dimethoxybenzoic acid¹⁶ (50 g) and sodium hydroxide (10 g) in water (500 ml) was hydrogenated over 0.5 g of palladium on carbon (5%) in a Parr low pressure hydrogenation apparatus. The pressure dropped to a constant value in 24 h. The catalyst was filtered off and the aqueous solution was extracted with ether (3 × 100 ml) to remove neutral components. Acidification and extraction with ether/ethyl acetate (5:1) gave a sample which was recrystallized from toluene (81%), m.p. 99–100°C (lit.¹⁷ 102°C).

5,6-Dimethoxy-1-indanol. To a solution of sodium borohydride (6 g) in ethanol (200 ml) was added 5,6-dimethoxy-1-indanone¹⁸ (40 g). The mixture was stirred for 24 h at room temperature. Water (800 ml) was added and the reaction mixture extracted with ethyl acetate (5 × 300 ml). The combined extracts were evaporated and the residue was used without further purification (96%).

5,6-Dimethoxyindene. To 5,6-dimethoxy-1-indanol (38.3 g) was added pyridine (10 ml) and acetic anhydride (100 ml) and the reaction mixture was boiled for 30 min. Then water (500 ml) was added and the mixture was extracted with methylene chloride (2 × 100 ml). The combined extracts were washed with water (3 × 200 ml), saturated potassium hydrogen carbonate solution (50 ml), and water (100 ml). After addition of acetone (100 ml) the solvent was evaporated and the residue distilled. The fraction boiling between 120 and 130°C/11 mmHg was collected. The crude product was contaminated with acetic acid which was removed by washing a methylene chloride solution of the substance with saturated KHCO₃ solution. Recrystallization from a mixture of ethanol/water (1:1) gave 20.8 g (60%) of the pure compound, m.p. 70–71°C (lit.^{4,5} 71–72°C), NMR (CDCl₃): δ 3.23 (p, 2 H, -CH₂^a-), 3.80 (s, 6 H, CH₃O-), 6.36 (p, 1 H, -CH^b=), 6.72 (p, 1 H, -CH^c=), and 6.88 and 6.92 (d, 2 H, Ar), *J*_{ab} 1.9, *J*_{bc} 5.7, *J*_{ac} 1.9, and *J*_{c-Ar} 0.9 Hz.

3-*t*-Butyl-5,6-dimethoxy-1-indanone. A mixture of β-*t*-butylacrylic acid¹⁹ (0.22 mol), veratrole (0.22 mol) and polyphosphoric acid (300 g) was kept at 60–70°C for 1 h. The cooled reaction mixture was mixed with water (100 ml), the temperature being kept below 50°C. Then the reaction mixture was poured into water (1000 ml) and partly neutralized with sodium hydroxide (100 g; *care: a violent reaction takes place*) whereafter the mixture was extracted with ethyl acetate (5 × 200 ml). The combined extracts were washed with sodium hydroxide solution (200 ml, 5 M) and with water and were then evaporated. The residue was distilled, the fraction boiling at 160–165°C/0.9 mmHg being collected. The yield was 86%. NMR (CDCl₃): δ 0.96 (s, 9 H, *t*-Bu),

2.66 (tr, 2 H, $-\text{CH}_2-$), 3.0–3.3 (p, 1 H, $-\text{CH}-$), 3.93 and 3.99 (d, 6 H, $\text{CH}_3\text{O}-$), and 6.92 and 7.20 (d, 2 H, Ar).

3-*t*-Butyl-5,6-dimethoxy-1-indanol. To a homogeneous solution of sodium borohydride (4 g) in absolute ethanol (150 ml) was added 5,6-dimethoxy-3-*t*-butyl-1-indanone (27 g). The reaction mixture was allowed to stand for 48 h and then poured into water (1000 ml). Extraction with ethyl acetate (5 × 200 ml) gave after evaporation 27 g (99 %) of the crude hydroxy compound. An IR spectrum of this material shows that all starting material had disappeared. The product was used in the next step without any further purification. NMR (CDCl_3): δ 1.04 (s, 9 H, *t*-Bu), 1.7–3.2 (p, 4 H, $-\text{CH}-$, $-\text{CH}-\text{CH}_2-$), 3.88 (s, 6 H, $\text{CH}_3\text{O}-$), 4.9–5.2 (q, 1 H, $-\text{CH}(\text{OH})-$), and 6.9 (s, 2 H, Ar).

1-*t*-Butyl-5,6-dimethoxyindene. To a slurry of sodium hydride (5 g; 50 % in oil) in ether (200 ml) was added crude 3-*t*-butyl-5,6-dimethoxy-1-indanol (27 g). The mixture was refluxed with stirring for 24 h. Carbon disulfide (9.2 g) was added to the cooled solution and the reaction mixture refluxed once more for 24 h. The solution was cooled again and methyl iodide (18 g) was added and the mixture refluxed for an additional 24 h. Water (200 ml) was added to this solution. The ether phase was separated from the water solution and the water phase once more extracted with ether (200 ml). The combined ether extracts were dried with magnesium sulfate and the ether was evaporated. The residue was distilled until a constant pressure of 11 mmHg was obtained. The temperature of the oil bath used was kept below 150 °C during this procedure. The product was then distilled at oil pump pressure, and the fraction boiling at 130–140 °C/1–1.5 mmHg was collected. Redistillation gave a yield of 10 g (40 %) of pure material which boiled at 130–132 °C/1 mmHg and solidified on standing. NMR (CDCl_3): δ (s, 9 H, *t*-Bu), 3.2 (q, 1 H, $-\text{CH}^a-$), 3.92 (s, 6 H, $\text{CH}_3\text{O}-$), 6.4 (q, 1 H, $-\text{CH}=\text{CH}^b-$), 6.75 (q, 1 H, $-\text{CH}^c=\text{CH}-$), and 7.16–6.90 (d, 2 H, Ar). $J_{ab}=J_{ac}=1.8$, $J_{bc}=5.8$, and $J_{c-Ar}=J_{a-Ar}=0.7$ Hz.

Anodic oxidation of 1-*t*-butyl-5,6-dimethoxyindene in concentrated solution. A solution of 1-*t*-butyl-5,6-dimethoxyindene (13.6 mmol) in HOAc/KOAc (1 M, 10 ml) was electrolysed with carbon electrodes until 0.85 F/mol of substrate had passed through the solution. To avoid severe filming the current direction was reversed every 25 s. The current density during the electrolysis was in the range of 1.0–2.0 mA/cm².

The electrolyte was poured into water (50 ml) and extracted with methylene chloride (2 × 20 ml). The combined extracts were washed with water (50 ml), saturated KHCO_3 solution (25 ml), and water (50 ml). Then acetone (100 ml) was added and the solvent

was evaporated to give 2.9 g of crude product (oil).

GLC analysis (3 % OV-25, 2 m × 3 mm, 140–300 °C/10 °C/min) of this oil revealed five main peaks. Peak 1 (30 %, 200 °C) was starting material, peak 2 (8 %, 220 °C) had a molecular weight of 248 (one oxygen atom added to 2; probably a hydroxy derivative), peaks 3 and 4 (2 %, 250 °C) were the 5,6-dimethoxy-3-*t*-butylindan-1,2-diol diacetates, and peak 5 corresponded to the dimer 7b (60 %, 300 °C). The total amount which passed the GLC detector was estimated to be 60 % of the sample.

The separation was done on a silica gel column with a mixture of $\text{CCl}_4/\text{CHCl}_3$ as eluent. The purest cyclodimer was obtained if the oil first was washed with cold (0 °C) hexane. Thus from 1.5 g of oil was 0.8 g washed off with 10 ml of hexane. The residue which consisted of 5 % starting material and 95 % dimeric and polymeric material, was eluted with a (9:1) mixture to give almost pure 7b (0.20 g).

Anodic oxidation of 1-*t*-butyl-5,6-dimethoxyindene (2) in dilute solution. A solution of 1-*t*-butyl-5,6-dimethoxyindene (4.31 mmol) in 25 ml of HOAc/KOAc (1 M) was electrolysed as described above until 1.66 F/mol of indene had passed through the solution. The electrode material was either carbon or platinum. The work-up procedure was the same as the one described above. The yield of crude product was 0.9 g.

GLC analysis of this showed very little starting material to be left (5 %) and two diacetates to be the major products together with a small proportion of dimeric compounds. The total amount which passed the GLC detector was estimated at 30 % of the sample.

The separation of the two diacetates from the residue was done on a silica gel column with a mixture of $\text{CCl}_4/\text{CHCl}_3$ as eluent. When the starting material and a small fraction of dimer 7b had been eluted with a 9:1 mixture the two diacetates were eluted with an 8:2 mixture. NMR (CDCl_3): δ 1.04 (s, 9 H, *t*-Bu), 2.08 (s, 6 H, $-\text{OCOCH}_3$), 3.87 (s, 6 H, $\text{CH}_3\text{O}-$), and 6.84 (s, 2 H, Ar). Shifts and coupling constants for the cyclopentane ring of diacetates 6b: δ 3.07 (H_a), 5.64 (H_b), and 6.26 (H_c), J_{ab} 2.0 and J_{bc} 5.4 Hz; δ 2.94 (H_a), 5.44 (H_b), and 5.96 (H_c), J_{ab} 2.0 and J_{bc} 1.5 Hz. From 1 g of starting material 0.15 g of diacetates was obtained. The residue was eluted with CHCl_3 . The material obtained showed no peak on GLC analysis and the NMR spectrum had only very broad signals indicating its polymeric nature.

A small fraction of the crude oil was boiled with acetic anhydride and pyridine before the separation procedure but no new diacetates were detectable (¹H NMR).

Anodic oxidation of 5,6-dimethoxyindene (1). A solution of 5,6-dimethoxyindene (42 mmol), KOAc (12 g), and HOAc (125 ml) was electro-

lysed as described for the *t*-butyl compound until 0.62 F/mol of substrate had been passed through the solution. The work-up procedure was the same as before. The yield was 8.3 g of a semi-crystalline product.

Dimeric and polymeric material was separated from unreacted starting material by washing with ether. The residue, which was almost pure dimer *7a*, was further purified by passing it through a silica gel column with $\text{CHCl}_3/\text{CCl}_4$ (1:9) as the eluent. The identification is described in the text.

Anodic oxidation of 5,6-dimethoxyindene (1) in dilute solution. A solution of 5,6-dimethoxyindene (2 mmol), KOAc (1 g), and HOAc (30 ml) was electrolysed as described above until 1.4 F/mol of substrate had passed through the solution. The work-up procedure was the same as before. The products were shown to be the two diacetates by GLC and MS (*m/e* 234; 2%; 192, 100%; in line with earlier experience^{1,2}). Attempts to purify the diacetates by silica gel chromatography were unsuccessful.

3-t-Butyl-5,6-dimethoxyindene. To a solution of 1-*t*-butyl-5,6-dimethoxyindene (100 mg) in ethanol (10 ml) potassium hydroxide (0.05 g) was added whereby a homogeneous solution was obtained. The mixture was allowed to stand for 48 h and then evaporated to dryness. To the solid residue water (10 ml) was then added and the solution extracted with ether (5 × 10 ml). The combined extracts together with dry acetone (50 ml) were evaporated to dryness. No work-up was necessary due to the completeness of the rearrangement. NMR (CDCl_3): δ 1.36 (s, 9 H, *t*-Bu), 3.21 (d, 2 H, $-\text{CH}_2-$), 3.87 (s, 3 H, $\text{CH}_3\text{O}-$), 3.92 (s, 3 H, $\text{CH}_3\text{O}-$), 6.09 (q, 1 H, $-\text{CH}=\text{}$), and 7.18–7.04 (d, 2 H, Ar), $J_{\text{CH}-\text{CH}_2}$ 1.9 Hz.

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