Sodium Methoxide Catalyzed Isomerization of Dimethyl 1-Oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates to Dimethyl 3-Oxo-1,7-indandicarboxylates

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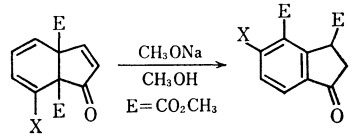
Treatment of dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates (**A**) with sodium methoxide in methanol gave particular dimethyl 3-oxo-1,7-indandicarboxylates (**F**). A multistep mechanism for the isomerization was proposed on the basis of the positional correlations between the dihydroindenones **A** and the corresponding isomers **F**. The isomerization seems to be initiated by the addition of a methoxide to the 1 position of the dihydroindenones **A** affording the cyclohexadienide anions (**B**), which cyclize to give dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,4-dicarboxylates (**C**). The dihydroindenones **C** become enolates (**D**), whose methoxycarbonyl group at the 3a position (E_9) shifts to the 1 position of the enolates of **F**, (**E**), with the aid of aromatization. The same treatment of methyl 3-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylates gave key information on the process for the isomerization of **A**.

Dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate (**1**) is a product of a thermal rearrangement of dimethyl 2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylate (dimethyl homobarrelenone-6,7-dicarboxylate).[1] During the course of investigation on the structure of **1**, it was found that the dihydroindenone is sensitive to sodium methoxide in methanol.[2] When a solution of **1** in methanol was added to a solution of sodium methoxide at 0 °C or at room temperature, the mixture immediately turned violet and then rapidly became pale yellow. The product, obtained in 95% yield, was dimethyl 3-oxo-1,7-indandicarboxylate (**2**). Under the same conditions the 7-methoxy derivative of **1**, (**3**), was isomerized to dimethyl 6-methoxy-3-oxo-1,7-indandicarboxylate (**4**).[2] This paper deals with an attempt to clarify the mechanism of isomerization.

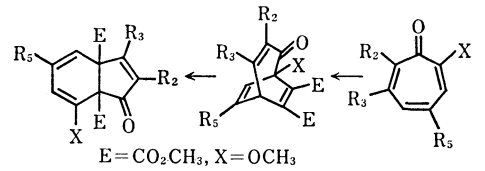


1 X=H **2** X=H
3 X=OCH_3 **4** X=OCH_3

Results and Discussion

Several alkyl derivatives of **3** were prepared and treated with sodium methoxide in methanol to examine the generality and limit of isomerization and the positional correlations between the *cis*-3a,7a-dihydroindenones and the products.

Dimethyl 2-isopropyl-7-methoxy-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate (**5**) is the product of a thermal rearrangement of dimethyl 3-isopropyl-1-methoxyhomobarrelenone-6,7-dicarboxylate (**5a**) derived by the regioselective Diels-Alder reaction of 7-isopropyl-2-methoxy-2,4,6-cycloheptatrien-1-one (7-isopropyl-2-methoxytropone, **5b**) with dimethyl acetylenedicarboxylate.[3] Similarly, dimethyl esters of 3-isopropyl- and 5-isopropyl-7-methoxy-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylic acids (**6** and **7**) were prepared from 6- and 4-isopropyl-2-methoxytropones (**6b** and **7b**) *via* the homobarrelenones (**6a** and **7a**), respectively.[3]



5 R_2=*i*-Pr, R_3=R_5=H **5a** **5b**
6 R_2=R_5=H, R_3=*i*-Pr **6a** **6b**
7 R_2=R_3=H, R_5=*i*-Pr **7a** **7b**

The conditions and results of the reactions of the *cis*-3a,7a-dihydroinden-1-ones with sodium methoxide in methanol are given in Table 1. A solution of **5** was added to a solution of sodium methoxide in methanol at room temperature (Run 5). The mixture soon turned reddish violet and then slowly became pale yellow. After being left to stand for 4 h, the solution was acidified and extracted promptly with three portions of dichloromethane. The product (**8**) is an isomer of **5** whose infrared spectrum shows a typical absorption due to the carbonyl of a 1-indanone, at 1691 cm^{-1}. The ultraviolet spectrum of **8** exhibits an absorption maximum of the electron transfer band at 270 nm, which is 25 nm longer than that of **2**. The difference suggests that **8** is one of the 5-methoxy-1-indanones.[4] The NMR spectrum of **8** indicates that the compound is dimethyl 2-isopropyl-6-methoxy-3-oxo-1,7-indandicarboxylate, showing an AB pattern at δ=7.10 and 7.88 (J=8.6 Hz) for H_5 (R_6) and H_4 (R_5), respectively, a doublet at δ=4.25 (J=3.4 Hz) for H_1 (R_3) and a doublet of doublets at δ=2.81 (J=4.1 and 3.4 Hz) for H_2.

Under the same conditions, **7** was isomerized to dimethyl 4-isopropyl-6-methoxy-3-oxo-1,7-indandicarboxylate (**9**) (Run 6), whose structure was deduced on the basis of its spectra.

3-Isopropyldihydroindenone **6** was inactive to sodium methoxide in methanol at room temperature (Run 7), whereas the isomer (**10**) was obtained when **6** and the base were heated under reflux in methanol (Run 8).

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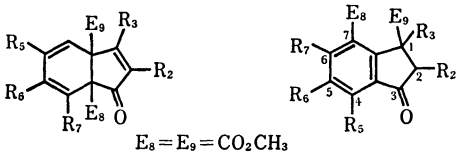
Product **10** has a characteristioc absorption maximum at 271 nm, its NMR spectrum showing an AB pattern at δ=7.05 and 7.93 (J=8.7 Hz) for H_5 (R_6) and H_4 (R_5), respectively, and AB pattern at δ=2.67 and 3.08 (J=19.2 Hz) for the *geminal* protons at the 2 position. Thus compound **10** should be dimethyl 1-isopropyl-6-methoxy-3-oxo-1,7-indandicarboxylate. The fact that **6** was isomerized to **10** seems to supply valuable information on the mechanism of the isomerization, but the reaction conditions were different from those for other dihydroindenones.

Table 1. A sodium methoxide catalyzed isomerization of dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates in methanol

Run	Dihydro-indenone	Conditions (temp, time)	Product	Yield[a] %
1	**1**[b]	0 °C, 5 min	**2**	95
2	**1**	r.t., 5 min	**2**	87
3	**1**	reflux, 10 min	**2**	74.5
4	**3**	r.t., 5 min	**4**	90
5	**5**	r.t., 4 h	**8**	96.5
6	**7**	r.t., 4 h	**9**	98
7	**6**	r.t., 12 h	—	95[c]
8	**6**	reflux, 12 h	**10**	63.4
9	**11**	r.t., 12 h	**13**	77
10	**12**	r.t., 12 h	—	95[c]
11	**12**	reflux, 12 h	**14**	74.5
12	**16**[d]	r.t., 4 h	**17**	70

a) After isolation. b) Ref. 2. c) Recovery. d) Methyl 4-methoxy-3-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylate.

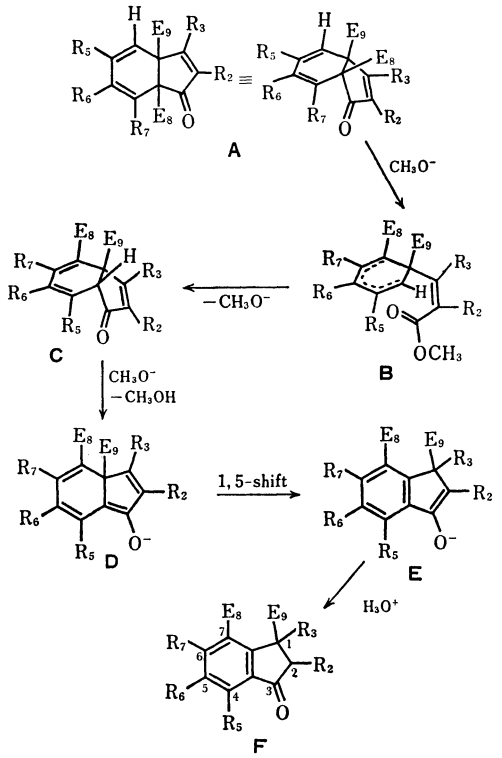


E_8=E_9=CO_2CH_3

5	R_2=*i*-Pr, R_3=R_5=R_6=H, R_7=OCH_3	**8**
6	R_3=*i*-Pr, R_2=R_5=R_6=H, R_7=OCH_3	**10**
7	R_5=*i*-Pr, R_2=R_3=R_6=H, R_7=OCH_3	**9**
11	R_3=CH_3, R_2=R_5=R_6=R_7H	**13**
12	R_3=CH_3, R_2=R_5=R_6=H, R_7=OCH_3	**14**
	E_8=CO_2CH_3, E_9=H	
16	R_2=R_3=R_5=R_6=H, R_7=OCH_3	**17**

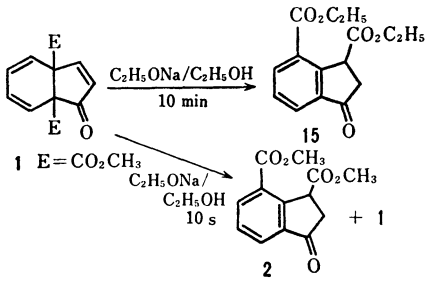
In order to know the generality of formation of dimethyl 1-alkyl-3-oxo-1,7-indandicarboxylates from the corresponding dimethyl 3-alkyl-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate, we developed a general synthetic method for 3-methyl-2-cyclopenten-1-ones from 2-cyclopenten-1-ones, prepared dimethyl 3-methyl-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates (**11** and **12**)[5] and treated them with sodium methoxide.

Isomerization of **11** proceeded at room temperature to give dimethyl 1-methyl-3-oxo-1,7-indandicarboxylate (**13**) (Run 9). The other 3-methyldihydroindenone **12** was not isomerized at room temperature, giving the somer (**14**) in boiling methanol (Runs 10 and 11, respectively). Thus dimethyl 3-alkyl-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates in general are isomerized with sodium methoxide to the corresponding dimethyl 1-alkyl-3-oxo-1,7-indandicarboxylates.



Scheme 1.

From the results we are able to estimate positional correlations between the dihydroindenones and the isomeric indanones. A mechanism for the isomerization is proposed as a working hypothesis which satisfies the positional correlations (Scheme 1). The mechanism shows that sodium methoxide acts as a catalyst in the first and second steps (**A** to **C**). To know the role of sodium methoxide in the reactions, **1** was teated with sodium ethoxide in ethanol. The reaction of **1** at room temperature for 10 min gave diethyl 3-oxo-1,7-indandicarboxylate (**15**) in 64.2% yield. The same reaction for 10 s afforded a mixture of **1** (recovered) and *dimethyl* 3-oxo-1,7-indandicarboxylate **2** in a 81 : 19 ratio. Thus, the alkoxides are shown to be the catalysts for the isomerization.



The tentative mechanism shows that E_9 of the dihydroindenones shifts to the 1 position of the indan-3-ones and E_8 of the former corresponds to the methoxycarbonyl group at the 7 position of the latter. For confirmation of the working hypothesis, either methyl ester of 1-oxo-*cis*-3a,7a-dihydroindene-3a- or 7a-carboxylic acid is necessary. We were able to prepare methyl 4-methoxy-3-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylate

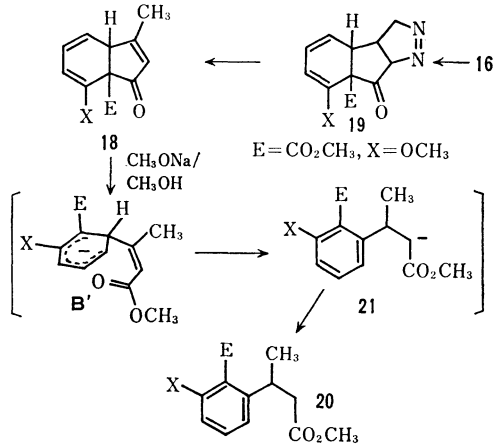
(**16**).[3]

When **16** was treated with sodium methoxide in methanol (Run 12), methyl 5-methoxy-1-oxo-4-indancarboxylate (**17**) was obtained in 70% yield. Thus, the methoxycarbonyl group at the 7a position of the dihydroindenones should correspond to that at the 7 position of the products, indan-3-ones.

Formation of the intermediate **B** is supported by the following results. When methyl 4-methoxy-1-methyl-3-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylate (**18**), derived from **16** *via* the pyrazoline (**19**), was treated with sodium methoxide in methanol, 1,2,3-trisubstituted benzene (**20**) was formed selectively. Its absorption spectra show that the compound is not methyl 5-methoxy-3-methyl-1-oxo-4-indancarboxylate. The ultraviolet spectrum does not exhibit the typical absorption maximum of 1-indanones, at *ca.* 300 nm. The infrared spectrum shows no absorption at *ca.* 1700 cm^{-1} due to the carbonyl of 1-indanones. The NMR spectrum of **20** indicates that the compound is methyl 3-(3-methoxy-2-methoxycarbonylphenyl)butanoate: the spectrum exhibits a doublet at $\delta=1.24$ (3H, $J=6.8$ Hz) for CH_3-(CH), an ABC pattern at $\delta=6.68$ (dd, $J=8.0$ and 0.9 Hz), 6.78 (dd, $J=8.0$ and 0.9 Hz) and 7.20 (t, $J=8.0$ Hz) for the three adjacent protons on the benzene ring, an ABC pattern at $\delta=2.34$ (dd, $J=15.0$ and 9.0 Hz), 2.59 (dd, $J=15.0$ and 5.6 Hz) and 3.14 (ddq, $J=9.0$, 5.6, and 6.8 Hz) for the $-CH_2-CH(CH_3)$ system, and three singlets at $\delta=3.54$ (3H), 3.73 (3H), and 3.81 (3H) for the methyl protons of the ether and the esters.

The process for formation of **20** should be addition of a methoxide to the 3 position of **18** giving the anion (**B'**), which corresponds to the intermediate **B** in Scheme 1, followed by aromatization to the intermediate (**21**).[6]

The reaction of dimethyl 4,7-dimethoxy-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate (**22**)[3] and sodium methoxide gave a mixture of several products which could not be separated.



The infrared spectrum of the mixture shows no typical absorption for the carbonyl of 1-indanones. If the working hypothesis is correct, **22**, would not give 1-indanones.

The fourth step of the mechanism (**D** to **E**) is the 1,5-shift of the methoxycarbonyl group and the aromatization. This type of migration of an alkoxycarbonyl group was observed on a cyclopentadiene skeleton.[7]

So far, the mechanism (Scheme 1) seems to be adequate for the isomerization of dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates to dimethyl 3-oxo-1,7-indandicarboxylates.

Experimental

General. Melting point were determined on a Thomas Hoover MP apparatus, and are uncorrected. Infrared spectra were recorded on Hitachi EPI-3 and Model 215 Spectrophotometers. Ultraviolet spectra were recorded on a Hitachi EPS-2T spectrometer. NMR spectra were obtained on Varian A-60 and HA-100 spectrometers equipped with spin decouplars, using tetramethylsilane as an internal standard. Mass spectral studies were conducted using a Hitachi RMU-6D spectrometer.

*Reaction of Dimethyl 1-Oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates with Sodium Methoxide in Methanol at Room Temperature.*

General Procedure: To a freshly prepared solution of sodium methoxide in methanol (100 mg of sodium and 10 ml of absolute methanol) was added rapidly a solution of the dihydroindenones (*ca.* 100 mg) in methanol (10 ml) at room temperature (on a water bath), and the mixture was allowed to stand for 5 min to 12 h. The reaction was quenched by 2 M-hydrochloric acid, diluted with water and extracted rapidly with three portions of dichloromethane (20 ml each). The extracts were combined, washed with two portions of water (20 ml each), dried over Na_2SO_4, and concentrated *in vacuo*. Isolation and purification of each product were performed with chromatography on silica gel and/or recrystallization.

*Reaction of Dimethyl 1-Oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates with Sodium Methoxide in Boiling Methanol. General Procedure*: A solution of sodium methoxide in methanol, prepared from 100 mg of sodium and 10 ml of methanol, was heated under reflux. To the solution was added a solution of the dihydroindenones (*ca.* 100 mg) in methanol (10 ml). After 10 min or 12 h reflux, the mixture was poured on a mixture of 2 M-hydrochloric acid and ice, and extracted with three portions of dichloromethane (20 ml each). The usual work-up followed by recrystallization or molecular distillation gave the 1-indanones.

Physical Properties of the New Dimethyl 3-Oxo-1,7-indandicarboxylates. Dimethyl trans*-2-Isopropyl-6-methoxy-3-oxo-1,7-indandicarboxylate (8)*: Colorless needles (from CH_3OH), mp 105—106 °C; UV_{max} (CH_3OH) 233 (log ε 4.28), 270 (4.16), and 296 nm (3.88); IR (KBr) 1725, 1691, 1581, and 814 cm^{-1}; NMR ($CDCl_3$) $\delta=0.85$ (3H, d, $J=7.0$ Hz, CH_3), 1.05 (3H, d, $J=7.0$ Hz, CH_3), 2.37 (1H, doublet of sept, $J=4.1$ and 7.0 Hz, $CH(CH_3)_2$), 2.81 (1H, dd, $J=4.1$ and 3.4 Hz), 3.68 (3H, s), 3.90 (3H, s), 3.97 (3H, s), 4.25 (1H, d, $J=3.4$ Hz, H_1), 7.10 (1H, d, $J=8.6$ Hz, H_5), and 7.88 (1H, d, $J=8.6$ Hz, H_4). Found: C, 63.68; H, 6.30%. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%.

Dimethyl 4-Isopropyl-6-methoxy-3-oxo-1,7-indandicarboxylate (9): Colorless needles (from ether–CH_3OH), mp 177–178 °C; UV_{max} (CH_3OH) 236 (log ε 4.41), 275 (4.17), and 300 nm $(3.69)^{sh}$; IR (KBr) 1728, 1698, 1597, and 1461 cm^{-1}; NMR ($CDCl_3$) $\delta=1.25$ (3H, d, $J=6.9$ Hz, CH_3), 1.27 (3H, d, $J=6.9$ Hz, CH_3), 2.84 (1H, dd, $J=18.2$ and 4.2 Hz, H_2-*cis* to C_1-ester), 2.92 (1H, dd, $J=18.2$ and 7.8 Hz, H_2-*trans* to C_1-ester), 3.67 (3H, s), 3.86 (3H, s), 3.95 (3H, s), 4.24 (1H, sept, $J=6.9$ Hz, $CH(CH_3)_2$), 4.47 (1H, dd, $J=7.8$ and 4.2 Hz, H_1), and 6.97 (1H, bs, $W_{1/2}=1.6$ Hz, H_5). Found: C,

63.51; H, 6.41%; M^+, 320. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%; M, 320.

*Dimethyl 1-Isopropyl-6-methoxy-3-oxo-1,7-indandicarboxylate(**10**)*: Colorless prisms (molecular distillation, bp 160 °C (bath)/0.2 Torr), mp 150—151 °C; UV_{max} (CH_3OH) 228 (log ε 4.31), 271 (4.20), 285 (4.10)^{sh}, and 294 nm (3.95)^{sh}; IR (KBr) 1735, 1709, 1581, 1470, and 828 cm^{-1}; NMR ($CDCl_3$) δ=0.51 (3H, d, J=6.8 Hz, CH_3), 1.03 (3H, d, J=6.8 Hz, CH_3), 2.67 (1H, d, J=19.2 Hz, H_2), 2.89 (1H, sept, J=6.8 Hz, $CH(CH_3)_2$), 3.08 (1H, d, J=19.2 Hz, H_2), 3.65 (3H, s), 3.93 (6H, s), 7.05 (1H, d, J=6 8 Hz, H_5), and 7.93 (1H, d, J=8.7 Hz, H_4). Found: C, 63.59; H, 6.29%; M^+, 320. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%; M, 320.

*Dimethyl 1-Methyl-3-oxo-1,7-indandicarboxylate (**13**)*: Colorless oil; UV_{max} (CH_3OH) 219 (log ε 4.51), 241 (4.01)$^{++}$, 292 (3.39), and 301 nm (3.39); IR (film) 1740, 1722, 1600, 1588, 1479, and 773 cm^{-1}; NMR ($CDCl_3$) δ=1.68 (3H, s, CH_3), 2.72 (1H, d, J=18.8 Hz, H_2), 2.98 (1H, d, J=18.8 Hz, H_2), 3.68 (3H, s), 3.91 (3H, s), 7.57 (1H, t, J=7.4 Hz, H_5), 7.99 (1H, dd, J=7.4 and 1.5 Hz, H_6 or H_4), and 8.35 (1H, dd, J=7.4 and 1.5 Hz, H_4 or H_6). Found: M^+, 262 Calcd for $C_{14}H_{14}O_5$: M, 262.

*Dimethyl 6-Methoxy-1-methyl-3-oxo-1,7-indandicarboxylate (**14**)*: Colorless needles (from CH_3OH), mp 118—119 °C; UV_{max} (CH_3OH) 228 (log ε 4.43), 271 (4.33), and 295 nm (4.13); IR (KBr) 1740^{sh}, 1732, 1713, 1706, 1581, and 824 cm^{-1}; NMR ($CDCl_3$) δ=1.60 (3H, s, CH_3), 2.60 (1H, d, J=18.5 Hz, H_2), 3.06 (1H, d, J=18.5 Hz, H_2), 3.67 (3H, s), 3.89 (3H, s), 3.97 (3H, s), 7.07 (1H, d, J=8.5 Hz, H_5), and 7.90 (1H, d, J=8.5 Hz, H_4). Found: C, 61.34; H, 5.49%; M^+, 292. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52%; M, 292.

*Reactions of Dimethyl 1-Oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate (**1**) with Sodium Ethoxide in Ethanol. A)*: To a solution of sodium ethoxide in ethanol, prepared from 100 mg of sodium and 10 ml of absolute ethanol, was added rapidly a solution of 98.8 mg (0.40 mmol) of **1** in 10 ml of ethanol, and the mixture was allowed to stand at room temperature for 10 min. The solution was poured on 2 M-hydrochloric acid (20 ml), diluted with water and extracted with three portions of dichloromethane (20 ml each). The usual work-up afforded 101 mg of red oil, which was chromatographed on silica gel. The product (71 mg, 64.2%) was identical with diethyl 3-oxo-1,7-indandicarboxylate (**15**) which was derived from **2** with sodium ethoxide in ethanol. **15**: Colorless needles (from ethanol), mp 78—80 °C; UV_{max} (CH_3OH) 218 (log ε 4.70), 240 (4.06)^{sh}, 265 (3.28)^{sh}, 290 (3.53), and 299 nm (3.55); IR (KBr) 1729, 1715, 1703, 1588, and 763 cm^{-1}; NMR ($CDCl_3$) δ=1.23 (3H, t, J=7.1 Hz), 1.39 (3H, t, J=7.1 Hz), 2.72 (1H, dd, J=19.2 and 4.4 Hz, H_2-*cis* to C_1-ester), 3.07 (1H, J=19.2 and 8.2 Hz, H_2-*trans* to C_1-ester), 4.19 (2H, q, J=7.1 Hz), 4.38 (2H, q, J=7.1 Hz), 4.71 (1H, dd, J=8.2 and 4.4 Hz, H_1), 7.55 (1H, t, J=7.4 Hz, H_5), 7.95 (1H, dd, J=7.4 and 1.5 Hz, H_6 or H_4), and 8.30 (1H, dd, J=7.4 and 1.5 Hz, H_4 or H_6). Found: C, 64.87; H, 5.74%; M^+, 276. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84%; M, 276.

B): To a solution of sodium ethoxide in ethanol, prepared from 150 mg of sodium and 10 ml of absolute ethanol, was added a solution of 104 mg of **1** in 10 ml of ethanol in one portion. After 10 s, 10 ml of 2 M-hydrochloric acid was added to the solution which was still violet. The mixture was extracted rapidly with three portions of dichloromethane (20 ml each). The usual work-up gave 108.1 mg of pale red oil, whose chromatography on silica gel gave 81 mg (77.9%) of **1** and 19 mg (18.3%) of dimethyl 3-oxo-1,7-indandicarboxylate **2**.

*Reaction of Methyl 4-Methoxy-3-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylate (**16**) with Sodium Methoxide in Methanol.* To a solution of sodium methoxide in methanol, freshly prepared from 150 mg of sodium and 15 ml of absolute methanol, was added a solution of 101.2 mg of **16** in 10 ml of methanol, and the mixture was allowed to stand at room temperature for 4 h. The usual work-up afforded pale red oil (81.3 mg), which was chromatographed on silica gel giving 71 mg (70 %) of methyl 5-methoxy-1-oxo-4-indancarboxylate (**17**), as colorless oil. **17**: UV_{max} (CH_3OH) 224 (log ε 4.48), 253 (3.92)^{sh}, and 303 nm (3.30); IR (film) 1723, 1692, and 1598 cm^{-1}; NMR ($CDCl_3$) δ=2.72 (2H, m, H_2), 3.12 (2H, m, H_3), 3.90 (3H, s), 4.02 (3H, s), 7.19 (1H, dt, J=8.0 and 0.5 Hz, H_6), and 7.95 (1H, d, J=8.0 Hz, H_7). 2,4-DNP of **17**: mp 221 °C (dec). Found: C, 53.75; H, 4.27; N, 13.90%. Calcd for $C_{18}H_{16}N_4O_7$: C, 54.00; H, 4.03; N, 14.00%.

*Preparation of Methyl 7-Methoxy-3-methyl-1-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylate (**18**).* To a solution of 473 mg (2.15 mmol) of **16** in 10 ml of ether was added an excess of an ethereal solution of diazomethane, and the mixture was allowed to stand overnight at room temperature. After removal of the excess of diazomethane and the solvent, crystallization of the residue gave 379 mg (67.3%) of the pyrazoline (**17**). A solution of 186.4 mg (0.71 mmol) of **17** in 5 ml of xylene was heated under reflux for 1 h. Removal of the solvent *in vacuo* followed by recrystallization from methanol gave 136 mg (0.52 mmol, 73%) of **18**. **17**: Colorless prisms (from CH_3OH), mp 150—151 °C (dec); IR (KBr) 1758, 1742, and 1653 cm^{-1}; Found: C, 59.51; H, 5.31; N, 10.71%. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68%. **18**: Colorless prisms (frm CH_3OH), mp 143—144 °C; IR (KBr) 1723, 1708, 1655, 1638, and 1599 cm^{-1}; NMR ($CDCl_3$) δ= 2.18 (3H, t, J=1.4 Hz, CH_3), 3.64 (3H, s), 3.73 (3H, s), 3.88 (1H, dddd, J=5.2, 2.2, 1.8, and 1.4 Hz, H_{7a}), 5.14 (1H, d, J=6.5 Hz, H_6), 5.51 (1H, dd, J=9.5 and 6.5 Hz, H_5), 5.99 (1H, ddd, J=9.5, 6.5, and 1.8 Hz, H_4), and 6.03 (1H, dq, J=2.2 and 1.4 Hz, H_2). Found: C, 66.51; H, 6.03%. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02%.

*Reaction of Methyl 7-Methoxy-3-methyl-1-oxo-*cis*-3a,7a-dihydroindene-3a-carboxylate (**18**) with Sodium Methoxide in Methanol.* To a solution of sodium methoxide in methanol, freshly prepared from 100 mg of sodium and 10 ml of absolute methanol, was added a solution of 135 mg (0.576 mmol) of **18** in 10 ml of methanol at room temperature, and the mixture was allowed to stand for 1 h. The usual work-up gave 149.7 mg (0.562 mmol, 97%) of methyl 3-(3-methoxy-2-methoxycarbonylphenyl)butanoate (**20**), as colorless oil which was purified by molecular distillation: 90—95 °C (bath)/0.06 Torr. **20**: UV_{max} 280 nm (log ε 3.43); IR (film) 1733, 1588, and 802 cm^{-1}. Found: C, 63.24; H, 6.94%; M^+, 266. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81%; M, 266.

References

1) a) T. H. Kinstle and P. D. Carpenter, *Tetrahedron Lett.*, **1969**, 3943; b) T. Uyehara, M. Funamizu, and Y. Kitahara, *Chem. Ind. (London)*, **1970**, 1500.

2) T. Uyehara, M. Funamizu, S. Miyakoshi, and Y. Kitahara, *Chem. Ind. (London)*, **1972**, 610.

3) T. Uyehara, S. Miyakoshi, and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **52**, 2023 (1979).

4) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, London (1964), p. 109.

5) T. Uyehara, S. Miyakoshi, and Y. Kitahara, *Synth. Commun.*, **3**, 365 (1973).

6) We have not investigated the process for the aromatization.

7) P. Schmidt, R. F. Hoffmann, and J. Baekes, *Angew. Chem. Int. Ed. Engl.*, **11**, 513 (1972).