Synthesis and Thermal Rearrangement of Homobarrelenones. Preparation of Dimethyl 1-Oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates

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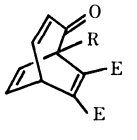
The Diels-Alder reaction of five derivatives of 2-methoxytropone with dimethyl acetylenedicarboxylate proceeds regiospecifically giving dimethyl 1-methoxy-2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylates, except in the case of 5-isopropyl-2-methoxytropone. The adducts undergo rearrangement selectively to dimethyl 7-methoxy-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates, upon heating under reflux in xylene. Regiochemical aspects of the cycloaddition and mechanistic aspects of the rearrangement are discussed.

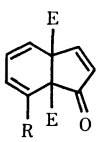
Tropone (2,4,6-cycloheptatrien-1-one, **1**) is known to react with various kinds of olefins giving Diels-Alder type 1,4-addition products.[1-12] Kinstle and Carpenter, and Uyehara *et al.* found independantly that **1** reacts with an acetylenic dienophile, dimethyl acetylenedicarboxylate (DMAD), to give dimethyl 6,7-dicarboxylate of bicyclo[3.2.2]nona-3,6,8-trien-2-one (homobarrelenone), (**2**).[13] The adduct is thermally labile, undergoing rearrangement selectively to dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate (**3**) upon heating under reflux in xylene.[13b] Dihydroindenone **3** is stable under acidic conditions, but is extreemly sensitive to the base, sodium methoxide.[14] When **3** was treated with the base in methanol at 0 °C, dimethyl 3-oxo-1,7-indandicarboxylate (**4**) was formed within a minute.

In order to know the mechanism of the rearrangement, we required a series of dimethyl 1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylates. There are two prerequisites for the synthesis of the dihydroindenones from tropones in practical yield: regioselective Diels-Alder reaction to give homobarrelenones and selective rearrangement of the adducts to the corresponding dihydroindenones.

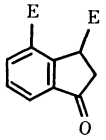
When 2-methoxytropone (**5**) was heated with DMAD at 90 °C, a regiospecific Diels-Alder reaction proceeded giving dimethyl 1-methoxyhomobarrelenone-6,7-dicarboxylate (**6**) in an excellent yield.[15] Similar specificity of the reaction positions of tropone **5** was observed for a reaction with methyl propiolate.[16] When the adduct **6** was heated under reflux in xylene, dimethyl 7-methoxy-1-oxo-*cis*-3a,7a-dihydroindene-3a,7a-dicarboxylate (**7**) was formed selectively.[15] These results prompted us to investigate a synthesis of the dihydroindenones from 2-methoxytropones.



2 R=H
6 R=OCH$_3$



3 R=H
7 R=OCH$_3$



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E=CO$_2$CH$_3$

Results and Discussion

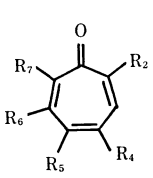
Diels-Alder Reaction of 2-Methoxytropones with Dimethyl Acetylenedicarboxylate (DMDA). 2-Methoxytropone **5** is obtained by careful treatment of tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) with diazomethane.[17] A series of alkyltropolones, 3-, 4-, and 5-isopropyl derivatives, is easily available.[18] Diazomethane treatment of 3-isopropyltropolone gives only 7-isopropyl-2-methoxytropone (**8d**).[19] A similar treatment of 4-isopropyltropolone gives a miture of 4- and 6-isopropyl-2-methoxytropones (**8a** and **8c**, respectively), which can not be separated from each other.[20] Compounds **8a** and **8c** have been prepared from 7-iodo-4-isopropyl and 3-iodo-6-isopropyl-2-methoxytropones, respectively, by catalytic hydrogenolysis.[21] 5-Isopropyl-2-methoxytropone (**8b**) is derived from 5-isopropyltropolone with diazomethane.[22]

The conditions and the results of the Diels-Alder reaction of 2-methoxytropones (**8a**—**8d**) with DMAD are given in Table 1. Each reaction temperature was kept as low as possible, since once a homobarrelenone derivative undergoes rearrangement to the corresponding dihydroindenone in the presence of DMAD, they react easily and a complex mixture of polysubstituted

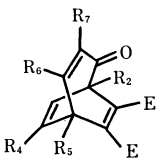
TABLE 1. PREPARATION OF THE HOMOBARRELENONES[a]

Tropone	Product	Yield (%)	Substituent				
			R_2	R_4	R_5	R_6	R_7
8a	**9a**	64.8[b]	OCH_3	*i*-Pr	H	H	H
8b	**9b**	96.5	H	*i*-Pr	H	H	OCH_3
8c	**9c**	63.0[c]	OCH_3	H	H	*i*-Pr	H
8d	**9d**	64.9	OCH_3	H	H	H	*i*-Pr
8e	**9e**	53.7[d]	OCH_3	H	OCH_3	H	H

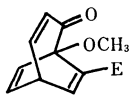
a) In a sealed tube, at 90 °C for 40 h. b) With 9.7% of **12a**. c) With 4.9% of **12c**. d) In a sealed tube, at 80 °C for 100 h, with 21.4% of **12e**.



8a—e



9a—e



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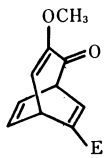

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E=CO$_2$CH$_3$

† Deceased February 4, 1976.

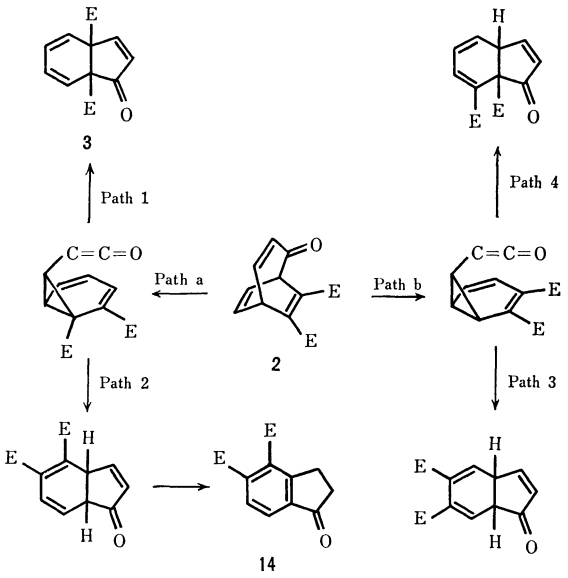
benzenes is formed.[12b,15] The structures of the addition products (**9a**, **9b**, **9c**, and **9d**) were deduced by means of their spectral data, mainly of the ^{1}H-NMR spectra.

Regioselectivity of the 1,4-additions is surprisingly high. DMAD underwent addition to **8a**, **8c**, and **8d** only at the 2,5-position, and to **8b** only at the 4,7-position. For explanation of the regiospecificity, we propose three major factors: 1) the difference between both primary interaction energies due to the methoxyl group, an electron-donating substituent; 2) the favorable secondary interaction between the ether oxygen of the tropones and the carbonyl carbon of the dienophile (an n-pi interaction); 3) the steric repulsion between the isopropyl group and the methoxycarbonyl group, in the transition states of addition.

Ethylene, a simple and symmetrical dienophile, underwent addition to 2-methoxytropone at 2,5- and 4,7-positions in the ratio of 87.7 and 12.3.[23] No secondary interaction would take place in the transition states leading to the adducts. The preferential addition of ethylene to the 2,5-position rather than to the 4,7-position was supported by the difference between the calculated interaction energies[23] by means of PMO equation proposed by Salem.[24] Maleic anhydride, a symmetrical dienophile, reacted with **5** only at the 2,5-position.[25] Thus, Diels-Alder type 1,4-addition of symmetrical dienophiles is favorable at the 2,5-position of 2-methoxytropone. Each isopropyl-2-methoxytropone could be regarded as a perturbed 2-methoxytropone. The difference between primary interaction energies of both reaction positions of **8a**, **8b**, **8c**, and **8d** with the dienophile should be similar to that of 2-methoxytropone with the dienophile.

Low regio- and stereoselectivities have been observed for the reactions of **5** and asymmetrical oleficic dienophiles, such as acrylonitrile and methyl acrylate.[3] However, methyl propiolate, an asymmetrical acetylenic dienophile, underwent addition regioselectively to **5** giving the adduct (**10**) in 67.5% yield with a small amount of the isomer (**11**).[16] Calculated interaction energies for the four possible regiochemical combinations of **5** and methyl propiolate suggest that the major product should be **11**. Disagreement with experimental results indicates that the regioselectivity can not be explained only by primary orbital interactions. In the transition state leading to **10**, the distance between the ether oxygen and the carbonyl carbon of the dienophile should be remarkably short, because of an acetylenic dienophile, and the secondary interaction between them could not be negligible. The same interaction seems to contribute to the selective addition of DMAD to the 2,5-position of 2-methoxytropones **5**, **8a**, **8c**, and **8d**.

Reversal of regiospecificity during the addition of DMAD to **8b** may be explained by large steric repulsion between the bulky isopropyl group and the methoxycarbonyl group in the transition state leading to the addition of the 2,5-position of **8b**, again because of the linear dienophile. This steric repulsion also contributes to the preferential formation of **9a** and **9d** from **8a** and **8d**, respectively.



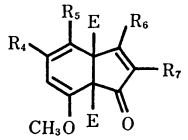
$E = CO_2CH_3$

Scheme 1.

Table 2. Thermal rearrangement of the homobarrelenones

Homobarrelenone	Product	Yield (%)
8a	**12a**[a]	74.1
8b	(**8b**)[a]	90.3[b]
	(**8b**)[c]	88.8[b]
8c	**12c**[a]	73.3
8d	**12d**[a]	63.0
8e	**12e**[a]	80.0
10	**17**[c]	74.9
15	**16**[a]	60.5
	16[c]	78.9

a) Heated under reflux in xylene for 40 h. b) Recovery. c) Gas-phase thermolysis at 350 °C/0.15 Torr.



12a $R_4 = i\text{-Rr}$, $R_5 = R_6 = R_7 = H$
12c $R_4 = R_5 = R_7 = H$, $R_6 = i\text{-Pr}$
12d $R_4 = R_5 = R_6 = H$, $R_7 = i\text{-Pr}$
12e $R_4 = R_6 = R_7 = H$, $R_5 = OCH_3$

$E = CO_2CH_3$

DMAD underwent addition to the 2,5-position of 2,5-dimethoxytropone (**8e**) giving the homobarrelenone (**9e**) with dihydroindenone (**12e**) even at 80 °C. Formation of **9e** reflects the contribution of that secondary interaction.

Thermal Rearrangements of the Homobarrelenones to cis-*3a,7a-Dihydroinden-1-ones.* The process of the thermal rearrangement of **2** to the dihydroindenone **3**, proposed by Kinstle and Carpenter, involves a [3,3]-sigmatropic shift to 7-*syn*-norcaradienylketene (**13**) followed by a [3,5]-sigmatropic shift (antarapfacial or Möbius) to **3**.[13a] If the mechanism is correct, there are four possible routes, each of them giving a paticular isomer as shown in Scheme 1. Preferential formation of **3** follows path a and path 1. Dimethyl 1-oxoindan-

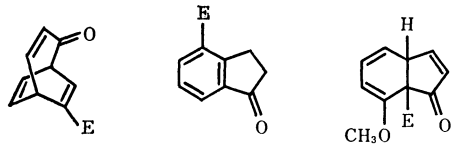
4,5-dicarboxylate (**14**), a minor product from **2**,[13b] should be formed through path a and path 2, followed by aromatization. Thus, preferential formation of **3** from **2** is interesting from a synthetic point of view. Study on the substituent effects for both sigmatropic rearrangements is of interest.

The rearrangement of **2** to **3** was performed by gas-phase[13a] or solution thermolysis.[13b] A concentrated solution of **2** gave many by-products, in the latter. The conditions and the results of the thermolysis of the homobarrelenones are given in Table 2. Compound **8b** was stable under the same conditions for the solution thermolysis of other isomers and at 350 °C *in vacuo*. Gas-phase thermolysis of **8b** at 450 °C gave unidentified decomposed products. The other homobarrelenones underwent rearrangement to the corresponding dihydroindenones through path a and path 1.

Thermal reactions of the monosubstituted homobarrelenone (**15**), derived from **1** and methyl propiolate,[16] yielded methyl 1-oxoindan-4-carboxylate (**16**). The process of the rearrangement involves path a and path 2 and aromatization. Gas-phase pyrolysis of **10** gave dihydroindenone (**17**). ^{1}H-NMR spectrum shows a multiplet at δ=3.97 (dddd, $J_{9,2}$=2.5 Hz, $J_{9,3}$=2.7, $J_{9,4}$=4.8, and $J_{9,5}$=1.7), a typical pattern of H_9 in *cis*-3a,7a-dihydroinden-1-ones.[26] The yield of **17** decreased when **10** was heated in a solution. The machanism of the process involves path a and path 1.

The regioselectivity of the [3,3]-sigmatropic shifts (path a is preferred) seems to be due to the electron-withdrawing substituents at the 8 and/or the 9 positions. The substituents should decrease the energy level of the HOMO of the acceptor radical fragment[27] in the transition state giving intermediates such as **13** through path a.

The other selective sigmatropic shifts (path 1 is preferred) may be caused by the differences between the pi-electron densities and the magnitude of the coefficients of each reaction position of the HOMO of the migrating framework.[27]



15 **16** **17**

E=CO_2CH_3

Experimental

General. Melting points 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. The mass spectral studies were conducted using a Hitachi RMU-6D spectrometer.

*2,5-Dimethyl-2,4,6-cycloheptatrien-1-one (**8e**).* Dimethyl sulfate (3.7 g) was added to a solution of 5-hydroxytropolone[28] (1.5 g) in 2 M-sodium hydroxide (20 ml) over a period of 2.5 h at 0 °C, and the mixture was stirred at room temperature for 2 h. After being heated under reflux for 30 min, the solution was cooled to room temperature, acidified (pH 5) with 10% hydrochloric acid and extracted with three portions of dichloromethane (20 ml each). The extracts were combined, dried ($MgSO_4$) and concentrated giving brown oil (1.6 g), a mixture of methoxytropones and **8e**. The mixture was dissolved in dichloromethane and treated with an ethereal solution of diazomethane. Evaporation of the solvents and crystallization from hexane–benzene gave pale yellow prisms (1.5 g, 83% yield). **8e**: mp 74—75 °C; IR (KBr) 1630, 1595, 1563, and 1518 cm^{-1}; NMR ($CDCl_3$) δ=3.86 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), and 6.35—7.27 (4H, m).

*Preparation of Homobarrelenone Derivatives (**9a**—**9e**). General Procedure*: Each 2-methoxytropone and DMAD (0.9—1.1 equiv) were placed in a Pyrex tube, sealed, and heated at 90±0.5 °C for 40 h (**8a**—**8d**) or at 80±0.5 °C for 100 h (**8e**). Isolation of each product was performed with chromatography on a silica-gel column or an alumina (neutral) column (for **9a** and **12a**) using gradient mixtures of benzene and ethyl acetate.

*Physical Properties of the New Homobarrelenones. A) Dimethyl 9-Isopropyl-1-methoxy-2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylate (**9a**)*: Pale yellow oil; UV_{max} (CH_3OH) 215 (log ε 4.13), 285 (3.15)^{sh} and 345 nm (2.60); IR (film) 1740, 1722, 1692, 1666, and 1640 cm^{-1}; NMR ($CDCl_3$) δ=1.11 (6H, d, J=7.0 Hz, $CH_3\times2$), 2.46 (1H, sept of d, J=7.0 and 1.5 Hz, $CH(CH_3)_2$), 3.61 (3H, s), 3.80 (3H, s), 3.84 (3H, s), 4.32 (1H, ddd, J=8.1, 1.5 and 0.9 Hz, H_5), 5.44 (1H, dd, J=10.8 and 0.9 Hz, H_3), 6.09 (1H, dd, J=1.5 and 1.5 Hz, H_8), and 7.15 (1H, dd, J=10.8 and 8.1 Hz, H_4). Found: M$^+$, 320.

*B) Dimethyl 9-Isopropyl-3-methoxy-2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylate (**9b**)*: Yellow oil; UV_{max} (CH_3OH) 227 (log ε 3.96), 289 (3.41) and 364 nm (2.58)^{sh}; IR (film) 1720, 1685, and 1640 cm^{-1}; NMR($CDCl_3$) δ=1.09 (6H, d, J=6.7 Hz, $CH_3\times2$), 2.49 (1H, broad sept, J=6.7 Hz, $CH(CH_3)_2$), 3.40 (3H, s), 3.74 (6H, s), 3.96 (1H, dd, J=9.5 and 2.3 Hz, H_5), 4.42 (1H, d, J=7.4 Hz, H_1), 5.98 (1H, ddd, J=7.3, 2.3 and 1.5 Hz, H_8), and 6.05 (1H, d, J=9.5 Hz, H_4). Found: M$^+$, 320.

*C) Dimethyl 4-Isopropyl-1-methoxy-2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylate (**9c**)*: Pale yellow oil; UV_{max} (CH_3OH) 224 (log ε 4.25), 287 (3.22)^{sh} and 335 nm (2.55)^{sh}; IR (film) 1740, 1720, 1678, 1658, and 1621 cm^{-1}; NMR ($CDCl_3$) δ=1.11 (3H, d, J=6.5 Hz, CH_3), 1.13 (3H, d, J=6.5 Hz, CH_3), 2.49 (1H, sept, J=6.5 Hz, $CH(CH_3)_2$), 3.53 (3H, s), 3.71 (6H, s), 4.37 (1H, ddd, J=6.0, 1.8 and 0.9 Hz, H_5), 5.01 (1H, dd, J=0.9 and 0.9 Hz, H_3), 6.56 (1H, dd, J=8.4 and 1.8 Hz, H_8), and 6.70 (1H, dd, J=8.4 and 6.0 Hz, H_9). Found: M$^+$, 320.

*D) Dimethyl 3-Isopropry-1-methoxy-2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylate (**9d**)*: Colorless needles (from CH_3OH), mp 107.5—108.5 °C; UV_{max} (CH_3OH) 222 (log ε 4.43), 292 (2.82)^{sh} and 362 nm (2.27); IR (KBr) 1729, 1715, 1672, 1657, and 1620 cm^{-1}; NMR ($CDCl_3$), δ=0.89 (3H, d, J=7.0 Hz, CH_3), 0.91 (3H, d, J=7.0 Hz, CH_3), 2.78 (1H, sept, J=7.0 Hz, $CH(CH_3)_2$), 3.59 (3H, s), 3.78 (3H, s), 3.82 (3H, s), 4.44 (1H, ddd, J=8.0, 6.5, and 1.2 Hz, H_5), 6.58 (1H, dd, J=8.5 and 1.4 Hz, H_8), 6.84 (1H, dd, J=8.0 and 1.2 Hz, H_4), and 6.88 (1H, dd, J=8.5 and 6.5 Hz, H_9). Found: C, 63.45; H, 6.29%; M$^+$, 320. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%; M, 320.

*E) Dimethyl 1,5-Dimethoxy-2-oxobicyclo[3.2.2]nona-3,6,8-triene-6,7-dicarboxylate (**9e**)*: colorless prisms (from CCl_4), mp 101–102 °C; UV_{max} (CH_3OH) 214 (log ε 3.90), 285

(2.85)^{sh} and 360 nm (1.91); IR (KBr) 1740, 1693, 1652, and 1620 cm^{-1}; NMR ($CDCl_3$) δ=3.45 (3H, s), 3.53 (3H, s), 3.78 (3H, s), 3.83 (3H, s), 5.24 (1H, d, J=11.8 Hz, H_3), 6.55 (1H, J=9.3 Hz, H_8), 6.97 (1H, d, J=9.3 Hz, H_9), and 7.07 (1H, d, J=11.8 Hz, H_4). Found: C, 58.61; H, 5.06%; M$^+$, 308. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23%; M, 308.

Thermal Rearrangements of Homobarrellenones. General Procedure. A) Solution Thermolysis: A solution of each homobarrelenone in dry xylene (0.04—0.046 M) was heated under reflux for 40 h. After removal of the solvent, purification of the product was performed by chromatography on a silica-gel column and/or by recrystallization.

B) Gas-phase Thermolysis: A sample of each homobarrelenone was placed in a goose-necked small flask attached to a 2×15 cm oven-heated Pyrex tube, placed obliquely (45°), packed with Pyrex tips. The other end of the tube was connected to a Dry-Ice trap. The end of the trap was connected to a vacuum pump. The system was evacuated (0.15—0.2 Torr), and the Pyrex tube was heated to 350 °C. The flask containing the sample was then heated with a nichrome wound heating jacket to 100—150 °C. The pyrolysate was purified by chromatography and/or recrystallization.

Physical Properties of the New cis-*3a,7a-Dihydroindenones. A) Dimethyl 5-Isopropyl-6-methoxy-1-oxo*-cis-*3a,7a-dihydroindene-3a,7a-dicarboxylate (**12a**)*: Colorless needles (from CH_3OH), mp 149—150 °C; UV_{max} (CH_3OH) 215 (log ε 4.13), 282 (3.61) and 347 nm (2.92); IR (KBr) 1725, 1704, 1658, and 1595 cm^{-1}; NMR ($CDCl_3$) δ=1.05 (3H, d, J=7.6 Hz, CH_3), 1.07 (3H, d, J=7.6 Hz, CH_3), 2.36 (1H, sept of d, J=7.6 and 2.0 Hz, $CH(CH_3)_2$), 3.48 (3H, s), 3.66 (3H, s), 3.68 (3H, s), 5.18 (1H, d, J=1.8 Hz, H_6), 5.19 (1H, dd, J=2.0 and 1.8 Hz, H_4), 6.45 (1H, d, J=5.8 Hz, H_2), and 7.43 (1H, d, J=5.8 Hz, H_3). Found: C, 64.03; H, 6.42%; M$^+$, 320. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%; M, 320.

B) Dimethyl 3-Isopropyl-7-methoxy-1-oxo-cis-*3a,7a-dihydroindene-3a,7a-dicarboxylate (**12c**)*: Colorless needles (from CH_3OH), mp 139–140 °C; UV_{max} (CH_3OH) 221 (log ε 4.16), 284 (3.57) and 338 nm (2.75); IR (KBr) 1732, 1705, 1655, and 1622 cm^{-1}; NMR ($CDCl_3$) δ=1.32 (3H, d, J=6.9 Hz, CH_3), 1.35 (3H, d, J=6.9 Hz, CH_3), 2.61 (1H, broad sept, J=6.9 Hz, $CH(CH_3)_2$), 3.67 (3H, s), 3.69 (3H, s), 3.70 (3H, s), 5.23 (1H, dd, J=6.5 and 0.8 Hz, H_6), 5.88 (1H, dd, J=10.0 and 0.8 Hz, H_4), 6.18 (1H, J=10.0 and 6.5 Hz, H_5), and 6.35 (1H, d, J=0.8 Hz, H_2). Found: C, 63.54; H, 6.38%; M$^+$, 320. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%; M, 320.

C) Dimethyl 2-Isopropyl-7-methoxy-1-oxo-cis-*3a,7a-dihydroindene-3a,7a-dicarboxylate (**12d**)*: Colorless needles (from CH_3OH), mp 123.5–124.5 °C; UV_{max} 220 (log ε 4.16), 283 (3.68) and 340 nm (2.86); IR (KBr) 1739, 1720, 1651, and 1594 cm^{-1}; NMR ($CDCl_3$) δ=1.03 (3H, d, J=7.1 Hz, CH_3), 1.16 (3H, d, J=7.1 Hz, CH_3), 2.76 (1H, sept of d, J=7.1 and 1.0 Hz, $CH(CH_3)_2$), 3.68 (9H, s), 5.23(1H, d, J=6.6 Hz, H_6), 5.52 (1H, d, J=10.0 Hz, H_4), 6.07 (1H, dd, J=10.0 and 6.6 Hz, H_5), and 7.01 (1H, d, J=1.0 Hz, H_3). Found: C, 63.73; H, 6.30%; M$^+$, 320. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%; M, 320.

D) Dimethyl 4,7-Dimethoxy-1-oxo-cis-*3a,7a-dihydroindene-3a,7a-dicarboxylate (**12e**)*: Pale yellow needles (from CH_3OH), mp 166—167 °C; UV_{max} (CH_3OH) 217 (log ε 4.00), 290 (3.73) and 365 nm (2.83); IR (KBr) 1746, 1712, 1662, and 1593 cm^{-1}; NMR ($CDCl_3$) δ=3.61 (3H, s), 3.66 (3H, s), 3.67 (3H, s), 3.71 (3H, s), 5.14 (2H, s, H_5 and H_6), 6.55 (1H, d, J=5.9 Hz, H_2), and 7.71 (1H, d, J=5.9 Hz, H_3). Found: C, 58.68; H, 5.09%; M$^+$, 308. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23%; M, 308.

E) Methyl 4-Methoxy-3-oxo-cis-*3a,7a-dihydroindene-3a-carboxylate (**17**)*: Colorless needles (from ether), mp 89—90 °C; UV_{max} (CH_3OH) 210 (log ε 4.10), 279 (3.63) and 344 nm (2.69); IR (KBr) 1736, 1704, 1651, and 1590 cm^{-1}; NMR ($CDCl_3$) δ=3.65 (3H, s) 3.72 (3H, s), 3.97 (1H, dddd, J=4.8, 2.7, 2.5, and 1.7 Hz, H_9), 5.17 (1H, d, J=6.7 Hz, H_6), 5.42 (1H, dd, J=9.7 and 4.8 Hz, H_4), 5.98 (1H, ddd, J=9.7, 6.7, and 1.7 Hz, H_5), 6.35 (1H, dd, J=5.7 and 2.5 Hz, H_2), and 7.49 (1H, dd, J=5.7 and 2.7 Hz, H_3). Found: C, 65.27; H, 5.53%; M$^+$, 220. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49%; M, 220.

*Methyl 1-Oxo-indan-4-carboxylate (**16**)*: Colorless needles (from CH_3OH), mp 102—103 °C; IR (KBr) 1710, 1580, and 760 cm^{-1}; NMR ($CDCl_3$) δ=2.70 (2H, m), 3.48 (2H, m), 3.95 (3H, s), 7.45 (1H, ddt, J=10.0, 10.0 and 0.75 Hz), 7.95 (1H, ddd, J=10.0, 1.3 and 0.5 Hz), and 8.27 (1H, dd, J=10.0 and 1.3 Hz). Found: M$^+$, 190.

*Hydrolysis of Methyl 1-Oxoindan-4-carboxylate (**16**)*. A mixture of a solution of **16** (100 mg) in dioxane (5 ml) and 2 M-sodium hydroxide (30 ml) was heated under reflux for 12 h, and washed with dichloromethane. The aqueous layer was acidified with 10% hydrochloric acid, and extracted with two portions of dichloromethane. Drying over $MgSO_4$, and concentration of the solution gave a reddish solid (83 mg), which was recrystallized from hot-water. The melting point and IR spectrum of the product, colorless needles (40 mg), were identical with those of 1-oxoindan-4-carboxylic acid:[29] mp 224.5—225.5 °C; IR (KBr) 3100, 1715 and 1687 cm^{-1}.

References

1) T. Nozoe, T. Mukai, T. Nagase, and Y. Toyooka, *Bull. Chem. Soc. Jpn.*, **33**, 1146 (1960).

2) a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, **1966**, 15; b) S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, **39**, 1351 (1966); c) S. Ito, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, **1970**, 2873; d) H. Tanida and H. R. Pfaendler, *Helv. Chim. Acta*, **55**, 3062 (1972).

3) a) S. Ito, H. Takeshita, and Y. Shoji, *Tetrahedron Lett.*, **1969**, 1815; b) Y. Shoji, Ph. D. Thesis, Tohoku University, Sendai, 1972.

4) M. Oda, M. Funamizu, and Y. Kitahara, *J. Chem. Soc., D*, **1969**, 737.

5) a) K. N. Houk and R. B. Woodward, *J. Am. Chem. Soc.*, **92**, 4145 (1970); b) T. Sasaki, K. Kanematsu, and T. Kataoka, *Chem. Lett.*, **1973**, 1183.

6) T. Uyehara and Y. Kitahara, *Chem. Ind.*, **1971**, 354.

7) S. Ito, H. Ohtani, S. Narita, and H. Homma, *Tetrahedron Lett.*, **1972**, 2223.

8) T. Uyehara, N. Sako, and Y. Kitahara, *Chem. Ind.*, **1973**, 41.

9) Y. Kashman and O. Awerbouch, *Tetrahedron*, **29**, 191 (1973).

10) Y. Fujise, Y. Chonan, H. Sakurai, and S. Ito, *Tetrahedron Lett.*, **1974**, 1585.

11) H. Takeshita, Y. Shoji, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 1041 (1974).

12) H. R. Pfaendler, H. Tanida, and E. Haselbach, *Helv. Chim. Acta*, **57**, 383 (1974).

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

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

15) T. Uyehara, M. Funamizu, and Y. Kitahara, *Chem. Ind.*, **1971**, 486.
16) T. Uyehara, S. Miyakoshi, and Y. Kitahara, *Chem. Ind.*, **1972**, 607.
17) T. Nozoe, S. Seto, T. Ikemi, and T. Arai, *Proc. Jpn. Acad.*, **27**, 102, (1951); J. W. Cook, A. R. Gibb, R. A. Raphael, and A. D. Somerville, *J. Chem. Soc.*, **1951**, 503; W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **73**, 828 (1951).
18) a) 3-Isopropyltropolone was derived from α-dolabrin easily prepared by the method of Asao and Kitahara: T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, **1970**, 89. b) 4- and 5-Isopropyltropolones were obtained from Takasago Perfumery Co., Ltd.
19) S. Seto, *Sci. Repts. Tohoku Univ., I*, **37**, 292 (1953).
20) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Proc. Jpn. Acad.*, **28**, 192 (1952).
21) M. Yasunami, Ph. D. Thesis, Tohoku University, Sendai, 1966.
22) T. Sato, *Tohoku Daigaku Hisuiyoeki Kenkyusho Hokoku*, **8**, 47 (1961).
23) T. Uyehara and Y. Kitahara, Abstr. No. 24-8c, 2nd International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, August 1970.
24) L. Salem, *J. Am. Chem. Soc.*, **90**, 543, 553 (1968).
25) T. Nozoe and Y. Toyooka, *Bull. Chem. Soc. Jpn.*, **34**, 623 (1961).
26) E. Baggldini, E. G. Herzog, S. Iwasaki, R. Scharta, and K. Schaffner, *Helv. Chim. Acta*, **30**, 277 (1967).
27) N. D. Epiotis, "Theory of Organic Reactions," Springer Verlag, New York (1978), pp. 11, 198.
28) M. Oda and Y. Kitahara, *Tetrahedron Lett.*, **1969**, 3295.
29) Y. Tomita, *Nippon Kagaku Zasshi*, **82**, 505 (1961).