

Synthesis of 2,5-Dioxacyclohepta[*jkl*]-*as*-indacenes

Takaaki Horaguchi*, Kazuhiro Miyazawa, Eietsu Hasegawa, and Takahachi Shimizu

Department of Chemistry, Faculty of Science, Niigata University, Ikarashi,
Niigata 950-21, Japan

Tsuneo Suzuki and Kiyoshi Tanemura

School of Dentistry at Niigata, The Nippon Dental University, Niigata, Hamaura-cho,
Niigata 951, Japan

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A variety of 2,5-dioxacyclohepta[*jkl*]-*as*-indacenes **5**, **7-14** were synthesized as a new heterocycle by the treatment of diethyl (5,9-dioxobenzocyclohepten-1,4-dioxy)diacetates **4a-e** with potassium hydroxide or sodium hydride in dioxane. The mechanism of furan-ring formation from **4a-e** was discussed.

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Introduction.

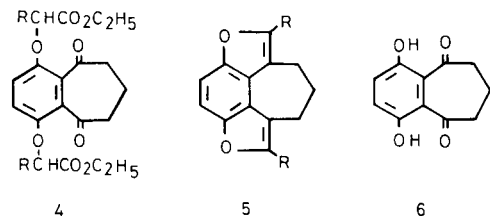
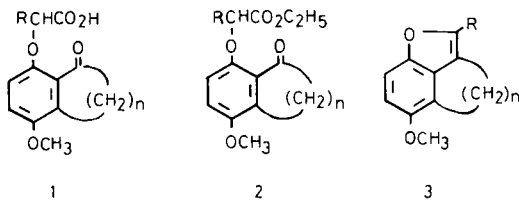
Benzofurans may be readily synthesized by the treatment under reflux with sodium acetate in acetic anhydride [2] of 2-acylphenoxyacetic acids or by heating of their esters with bases such as potassium hydroxide [3] or sodium hydride [4]. When the methods were applied to acids **1** ($n = 3, 4$) and esters **2** ($n = 3, 4$) having six- or seven-membered carbonyl group, naphtho[1,8-*bc*]furans **3** ($n = 3$) [5] or cyclohepta[*cd*]benzofurans **3** ($n = 4$) [1] were obtained. Although the yield of furans **3** ($n = 3, 4$) was not necessarily good compared with that of benzofuran synthesis because the carbonyl group in the six- or seven-membered ring could not rotate freely to take a favorable conformation for furan-ring formation, potassium hydroxide and sodium hydride were effective for furan-ring formation from

cyclic ketones. In this paper, we use diethyl (5,9-dioxobenzocycloheptene-1,4-dioxy)diacetates **4** as starting materials to synthesize new heterocyclic compounds, 2,5-dioxacyclohepta[*jkl*]-*as*-indacenes **5** or their derivatives. Compounds **5** have two furan-rings condensed at the *peri*-positions and may have strain in the molecule. However, it seems that the strain is not so large because a seven-membered cyclic ketone is more flexible than a six-membered cyclic ketone [6].

Results and Discussion.

Starting esters **4** were prepared from the reactions of cyclic diketone **6** [7] with ethyl bromoacetate or its derivatives. The results are summarized in Table 1. When **6** reacted with ethyl bromoacetate in the presence of potassium carbonate an ester **4a** was obtained in 55% yield. Similarly, the reaction of **6** with ethyl 2-bromopropionate gave **4b** in 62% yield. The ¹H nmr spectrum of **4b** suggests that it was a 1:1 mixture of *dl* and *meso* isomers. Recrystallization of the mixture gave one pure isomer of the two. It is not clear which isomer was obtained in the pure state. Reaction of **6** with ethyl 2-bromobutyrate, ethyl 2-bromo-3-methylbutyrate, or ethyl 2-bromo-2-phenylacetate afforded the corresponding esters **4c-e**. The esters **4c-e** were a 1:1 mixture of *dl* and *meso* isomers respectively judging from the nmr spectra and hplc analysis. Re-

Formula 1



- a ; R = H
b ; R = CH₃
c ; R = C₂H₅
d ; R = CH(CH₃)₂
e ; R = Ph

Table 1
Reactions of Diketone **6** with Ethyl Bromoacetate Derivatives
RCHBrCO₂C₂H₅ in the Presence of Bases

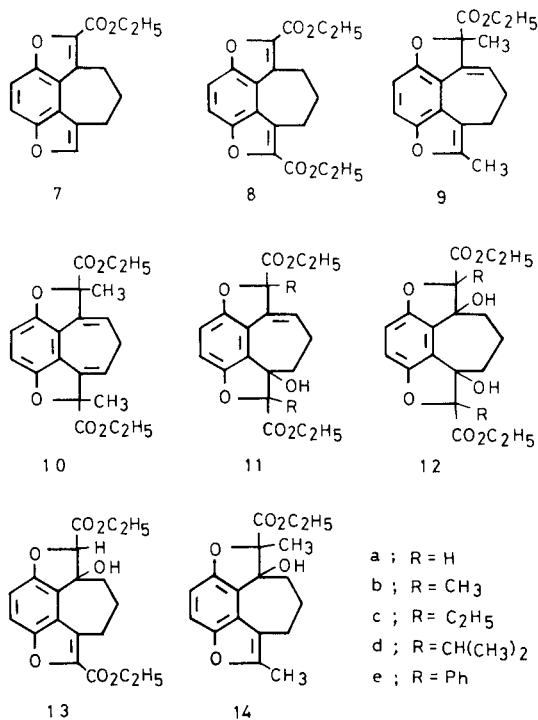
Product	Base	Solvent	Temperature	Time, hours	Yield (%)
4a	K ₂ CO ₃	Dioxane	Reflux	9	55
4b [a]	K ₂ CO ₃	Dioxane	Reflux	16	62 [b]
4c [a]	K ₃ PO ₄	Dioxane	Reflux	8	62 [b]
4d	K ₃ PO ₄	DMSO	60°	6	35 [b]
4e	K ₃ PO ₄	Dioxane	30°	3.5	51 [b]

[a] Recrystallization of a mixture of *dl* and *meso* isomers from benzene-hexane gave one pure isomer. [b] Yields of a mixture of *dl* and *meso* isomers.

crystallization of **4c** afforded one pure isomer of the two. However, compounds **4d** and **4e** were used as a mixture of *dl* and *meso* isomers for furan-ring formation because of oily products. Next we attempted to prepare carboxylic acids by hydrolysis of esters **4** for the reaction with sodium acetate in acetic anhydride. Unfortunately, the carboxylic acids produced were not isolated because they were too soluble in water.

Initially, reactions of esters **4** with potassium hydroxide in dioxane were examined. The results are summarized in Table 2 and the structures of products are shown in Formula 2. When a mixture of **4a** (R = H), potassium hydroxide, and dioxane was refluxed for 2.5 hours, then poured into 2*M* hydrochloric acid, three products of **5a**, **7**, and **8** were obtained. The major product was compound **8** (72%). In the case of **4b** (R = CH₃) four products of **5b**, **9**, **10**, and **11b** were isolated and compound **11b** (55%) was the major product. On the other hand, ester **4c** (R = C₂H₅) gave **5c** and **11c** in poor yields. When **4d** (R = CH(CH₃)₂) was allowed to react no product was obtained because of saponification of the starting ester. Compound **4e** (R = Ph) afforded **5e** (43%) and **12e** (33%). The results suggest that seven-membered ring is flexible enough to prepare two furan rings at the *peri*-positions and that basicity of potassium hydroxide is not strong enough to form a furan ring from **4c** and **4d**. For compounds **10-12** several stereoisomers are possible, however, only one isomer was obtained in every reaction. The stereochemistry of each compound is not clear.

Formula 2

Table 2
Reactions of Esters **4a-e** with Potassium Hydroxide in Dioxane [a]

Compound	Product (Yield, %)			
4a	5a (11)	7 (8)	8 (72)	
4b	5b (5)	9 (13)	10 (8)	11b (55)
4c	5c (2)	11c (13)		
4d [b]				
4e	5e (43)	12 (33)		

[a] A mixture of **4** (1.80 mmoles), potassium hydroxide (0.504 g, 9.00 mmoles), and dioxane (10.0 ml) was refluxed for 2.5 hours. The mixture was poured into 2*M* hydrochloric acid (100 ml) and stirred for 0.5 hour. [b] Compound **4d** was saponified and no product was obtained.

To examine the mechanism of furan-ring formation the reaction mixture of **4** and potassium hydroxide was divided into the precipitate and the solution by filtration. The precipitate was treated with 2*M* hydrochloric acid and extracted with ether. The solution was extracted with ether without acidification. The results are summarized in Table 3. In the case of **4a**, compounds **5a** and **7** which had lost ethoxycarbonyl groups were obtained from the precipitate and compounds **8**, **12a**, and **13** which had two ethoxycarbonyl groups were isolated from the solution. The same treatment of the reaction mixture of **4b** and potassium hydroxide gave similar results. It shows that the precipitates were potassium salts of carboxylic acids and converted to **5a-b** or **7** by decarboxylation after acidification [8] and that alcohols **12a-b**, **13**, and **14** were readily dehydrated with hydrochloric acid to form carbon-carbon double bonds in the furan ring or seven-membered ring. In fact, stirring of **12a** in 2*M* hydrochloric acid for 0.5 hour afforded **8** in 79% yield. Similar treatment of **12b** with hydrochloric acid gave **10** and **11b** in 4 and 53% yields respectively. Furthermore, in the reaction of **12a** with potassium hydroxide, **5a** (14%) was obtained from the precipitate, and **8** (11%) and **13** (35%) were isolated from the solution. By the similar treatment of **12b** with potassium hydroxide, **5b** (19%) was obtained from the precipitate and **14** (5%) was isolated from the solution.

Table 3
Reactions of Esters **4a-b** with Potassium Hydroxide in Dioxane (Separate Treatment of Precipitate and Solution) [a]

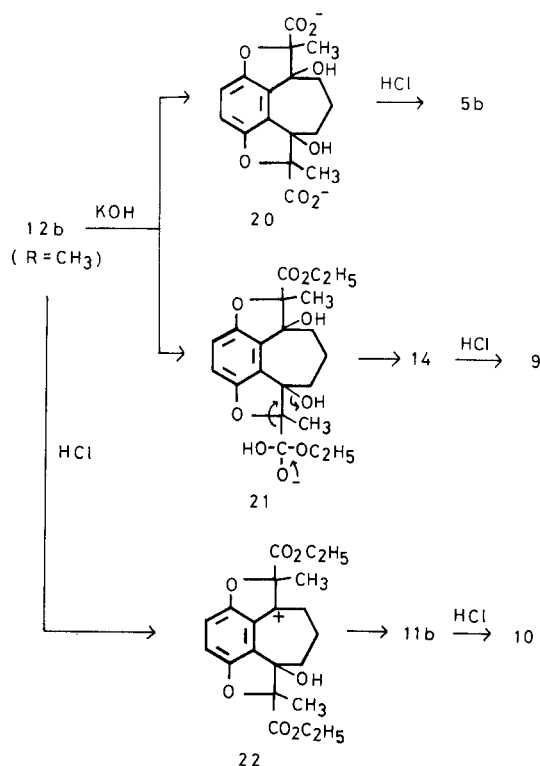
Compound	Product from precipitate (yield, %)		Product from solution (yield, %)		
4a	5a (11)	7 (4)	8 (15)	12a (26)	13 (22)
4b	5b (10)		12b (60)	14 (18)	

[a] A mixture of **4** (1.80 mmoles), potassium hydroxide (0.504 g, 9.0 mmoles), and dioxane (10.0 ml) was refluxed for 2.5 hours. The mixture was divided into the precipitate and the dioxane solution by filtration. The precipitate was extracted after acidification with hydrochloric acid and the dioxane solution was extracted without acidification.

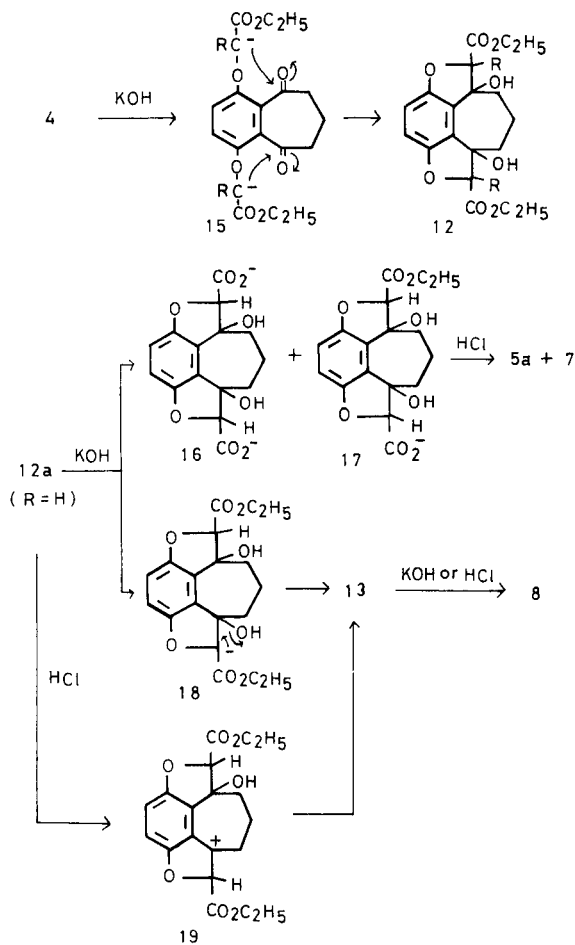
From the above results a plausible mechanism of furan-ring formation using potassium hydroxide is shown in Scheme 1. Potassium hydroxide abstracts hydrogens adja-

cent to ethoxycarbonyl groups in **4** to give an anion **15**. The anion **15** attacks the carbonyl carbons of seven-membered ring to afford furan **12**. In the case of $R = H$, compound **12a** is partly saponified with potassium hydroxide to give salts **16** and **17**. The salts **16** and **17** are converted to **5a** and **7** by elimination of carbon dioxide after acidification. Compound **12a** is readily dehydrated by potassium hydroxide through an anion such as **18** to afford products **13** and **8**. Dehydration of **12a** also occurs with hydrochloric acid to give **8** through a cation such as **19**. In the case of $R = CH_3$, **12b** is converted to a salt **20** by saponification with hydroxide ion or to **14** through elimination of ethyl carbonate and hydroxide ion from **21**. Compounds **20** and **14** are then converted to **5b** and **9** respectively after acidification. Compound **12b** is also dehydrated with hydrochloric acid to **11b** or **10** through a cation such as **22**. The reactions of **4c-e** with potassium hydroxide would proceed by the same mechanism.

Secondly, reactions of **4** with sodium hydride in dioxane were examined. The results are summarized in Table 4. When a mixture of **4a**, sodium hydride, and dioxane was



Scheme 1



refluxed for 1 hour and poured into *2M* hydrochloric acid, esters **7** (10%) and **8** (68%) were obtained. In contrast, reactions of **4b-e** afforded furans **5b-e** (66, 55, 41, 66%) which have no ethoxycarbonyl group as major products. The minor products were compounds **12b-d**. Though several stereoisomers were possible for **12b-d** only one product was obtained in each reaction.

Table 4

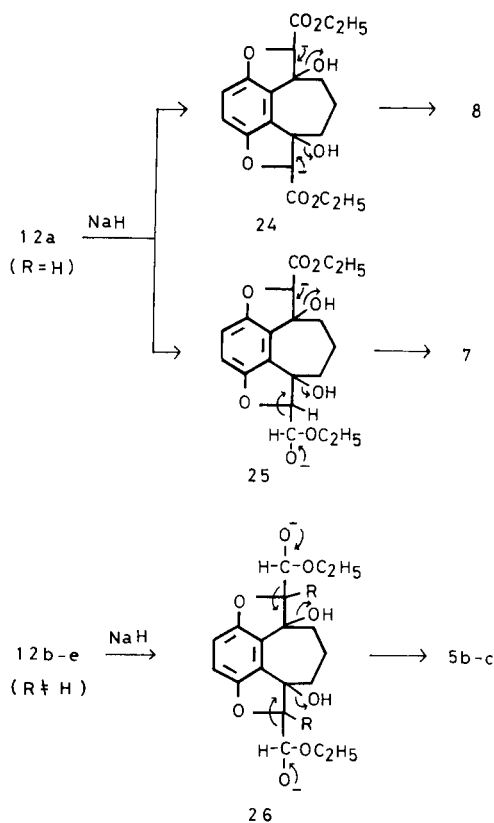
Reactions of Esters **4a-e** with Sodium Hydride in Dioxane [a]

Compound	Product (Yield, %)	
4a	7 (10) [b]	8 (68) [b]
4b	5b (66)	12b (4)
4c	5c (55)	12c (34)
4d	5d (41)	12d (6)
4e	5e (66)	12 (0) [c]

[a] A mixture of **4** (1.80 mmoles), 60% sodium hydride (0.360 g, 9.00 mmoles), and dioxane (10.0 ml) was refluxed for 1 hour. The mixture was poured into *2M* hydrochloric acid (100 ml) and stirred for 15 minutes. [b] Using **4a** as the starting material, esters **7** and **8** were obtained in place of **5a** and **12a** because of facile dehydration in the furan ring. [c] Compound **12e** was not obtained.

To examine the mechanism of furan-ring formation the reaction mixture of **4a** and sodium hydride was divided into the precipitate and the solution by filtration. The precipitate gave no product after acidification. Analysis (tlc) of the solution showed that compounds **7** and **8** were already present in the solution before acidification. Similar results were obtained for the reaction of **5b** and sodium hydride. From the results a plausible mechanism of furan-ring formation using sodium hydride is shown in Scheme 2.

Scheme 2



Compounds **4** are converted to **12** in a manner similar to the reactions of **4** and potassium hydroxide. In the case of R = H, sodium hydride abstracts methylene hydrogens in the furan ring of **12a** to afford an anion **24** which produces **8** by elimination of hydroxide ion. On the other hand, sodium hydride attacks the carbonyl carbon of **12a** to give **25** which produce **7** by elimination of ethyl formate and hydroxide ion. In the case of R ≠ H, there is no hydrogen to abstract in the furan ring. Therefore, sodium hydride attacks only the carbonyl carbon of **12b-e** to give **26** which are converted to **5b-e**. In fact, the reaction of **12b** with sodium hydride afforded **5b** in 72% yield.

Thus, potassium hydroxide and sodium hydride are useful bases for preparation of a variety of 2,5-dioxacyclohepta[*ijkl*]-as-indacene derivatives.

EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. 1,4-Dioxane was dried by refluxing with sodium. The ir spectra were determined on a Hitachi Model 270-30 ir spectrometer. The ¹H and ¹³C nmr spectra were determined at 90 MHz on a JEOL JNM-FX 90Q FT NMR spectrometer, using tetramethylsilane as the internal standard.

General Procedure for the Reactions of **4a-e** with Potassium Hydroxide in Dioxane.

A mixture of **4** (1.80 mmoles), powdered potassium hydroxide (0.504 g, 9.00 mmoles), and dioxane (10.0 ml) was refluxed for 2.5 hours. The mixture was poured into 2M hydrochloric acid (100 ml), stirred for 0.5 hour at room temperature, and extracted with ether. The extract was washed with a 1M aqueous potassium carbonate solution, then with water, dried, and evaporated. The residue was chromatographed and eluted by changing eluent from benzene to benzene-ether or benzene-acetone. The first fraction gave **5** and the last fraction afforded **12**. The other products **7-11** were isolated from the middle fraction.

General Procedure for the Reactions of **4a-b** with Potassium Hydroxide in Dioxane (Separate Treatment of Precipitate and Solution).

A mixture of **4** (1.80 mmoles), powdered potassium hydroxide (0.504 g, 9.00 mmoles), and dioxane (10.0 ml) was refluxed for 2.5 hours. After filtration of the precipitate the filtrate was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted by changing eluent from benzene to benzene-ether or benzene-acetone to give products **8**, **12**, **13**, and **14**. The precipitate was poured into 2M hydrochloric acid (100 ml) and stirred for 0.5 hour at room temperature. The resulting products were extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene to give products **5** and **7**.

General Procedure for the Reactions of **4a-e** with Sodium Hydride in Dioxane.

A mixture of **4** (1.80 mmoles), 60% sodium hydride (0.360 g, 9.00 mmoles), and dioxane (10.0 ml) was refluxed for 1 hour. The mixture was decomposed by adding 2M hydrochloric acid (100 ml) and stirring for 15 minutes. The products were extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted first with benzene(4)-hexane(1) to remove coating oil of sodium hydride. Further elution with benzene, benzene-ether, or benzene-acetone gave compounds **5**, **7**, **8**, and **12**.

Reaction of **12a** with Hydrochloric Acid.

Compound **12a** (0.34 g, 0.90 mmole) in dioxane (10.0 ml) was poured into 2M hydrochloric acid (50 ml) and the mixture was stirred for 0.5 hour at room temperature. The resulting products were extracted with ether. The extract was washed with a 2M aqueous potassium carbonate solution, then with water, dried, and evaporated. The residue was chromatographed and eluted with benzene(4)-ether(1) to give **8** (0.244 g, 79%).

Reaction of **12b** with Hydrochloric Acid.

Compound **12b** (0.37 g, 0.90 mmole) in dioxane (10.0 ml) was poured into 2M hydrochloric acid (50 ml) and the mixture was stirred for 1 hour at room temperature. The following treatment was carried out in a manner similar to the reaction of **12a** to give **10** (0.013 g, 4%) and **11b** (0.186 g, 53%).

Reaction of **12b** with Sodium Hydride in Dioxane.

A mixture of **12b** (0.37 g, 0.90 mmole), 60% sodium hydride (0.180 g, 4.50 mmoles), and dioxane (10.0 ml) was refluxed for 1 hour. To the mixture 2M hydrochloric acid (50 ml) was added and

it was stirred for 15 minutes at room temperature. The mixture was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted first with benzene(4)-hexane(1) to remove coating oil of sodium hydride. Further elution with benzene gave **5b** (0.144 g, 72%).

1,4-Dihydroxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-5,9-dione **6**.

This compound was prepared in 45% yield according to literature [7], yellow plates from benzene-hexane, mp 147.5-148° (lit [7], mp 149°); ir (potassium bromide): 1630 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 2.19 (quintet, J = 7 Hz, 2H, CH₂CH₂CH₂), 2.91 (t, J = 7 Hz, 4H, CH₂CH₂CH₂), 7.14 (s, 2H, Ar-H₂), 11.52 (s, 2H, OH and OH); ¹³C nmr (deuteriochloroform): δ 19.2 (t), 42.0 (t), 118.2 (s), 127.3 (d), 155.0 (s), 204.4 (s).

Diethyl (5,9-Dioxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1,4-diyloxy)diacetate **4a**.

A mixture of **6** (5.00 g, 24.3 mmoles), ethyl bromoacetate (16.2 g, 7.19 mmoles), potassium carbonate (13.4 g, 97.1 mmoles), and dioxane (50.0 ml) was refluxed for 9 hours. During reflux potassium carbonate (2.00 g, 14.5 mmoles) was added every 2 hours. After removal of the potassium carbonate by filtration the dioxane was evaporated and the residue was extracted with ether. The extract was washed, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene to remove ethyl bromoacetate. Further elution with benzene(7)-ether(3) gave **4a** (6.10 g, 66%); it formed colorless needles from benzene-hexane, mp 135-136°; ir (potassium bromide): 1750 (CO₂C₂H₅), 1690 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.28 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.94-2.22 (m, 2H, CH₂CH₂CH₂), 2.81 (t, J = 6 Hz, 4H, CH₂CH₂CH₂), 4.23 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 4.63 (s, 4H, CH₂CO₂ and CH₂CO₂), 6.99 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 14.1 (q), 18.9 (t), 43.2 (t), 61.3 (t), 68.2 (t), 118.4 (d), 129.8 (s), 149.3 (s), 168.7 (s), 202.3 (s).

Anal. Calcd. for C₁₉H₂₂O₆: C, 60.31; H, 5.86. Found: C, 60.48; H, 5.99.

Diethyl 2,2'-(5,9-Dioxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1,4-diyloxy)dipropionate **4b**.

A mixture of **6** (5.00 g, 24.3 mmoles), ethyl 2-bromopropionate (17.4 g, 96.1 mmoles), potassium carbonate (13.4 g, 97.1 mmoles), and dioxane (50.0 ml) was refluxed for 16 hours. During reflux potassium carbonate (2.00 g, 14.5 mmoles) was added every 2 hours. After removal of the potassium carbonate by filtration the dioxane was evaporated. The residue was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene to remove ethyl 2-bromopropionate. Further elution with benzene(7)-ether(3) gave **4b** (6.10 g, 62%) as a mixture (1:1 ratio) of *dl* and *meso* isomers. Recrystallization from benzene-hexane afforded one pure product (2.10 g, 22%) of the two as colorless needles, mp 121-122°; ir (potassium bromide): 1750 (CO₂C₂H₅), 1700 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.25 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.56 (d, J = 7 Hz, 6H, CH₃CHCO₂ and CH₃CHCO₂), 1.91-2.16 (m, 2H, CH₂CH₂CH₂), 2.66-2.92 (m, 4H, CH₂CH₂CH₂), 4.19 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 4.67 (q, J = 7 Hz, 2H, CH₃CHCO₂ and CH₃CHCO₂), 6.94 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 14.1 (q), 18.3 (q), 19.1 (t), 43.3 (t), 61.2 (t), 76.2 (d), 119.4 (d), 130.4

(s), 149.1 (s), 171.8 (s), 202.1 (s).

Anal. Calcd. for C₂₁H₂₆O₆: C, 62.06; H, 6.45. Found: C, 61.78; H, 6.38.

Diethyl 2,2'-(5,9-Dioxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1,4-diyloxy)dibutyrate **4c**.

A mixture of **6** (2.00 g, 9.71 mmoles), ethyl 2-bromobutyrate (5.70 g, 29.2 mmoles), tripotassium phosphate (6.20 g, 29.2 mmoles), and dioxane (20.0 ml) was refluxed for 8 hours. During reflux tripotassium phosphate (1.00 g, 4.72 mmoles) was added every 2 hours. After removal of the tripotassium phosphate by filtration water was added to the filtrate. The resulting precipitate was collected by filtration, chromatographed, and eluted with benzene(7)-ether(3) to give **4c** (2.60 g, 62%) as a mixture (1:1 ratio) of *dl* and *meso* isomers. Recrystallization from benzene-hexane gave one pure product (1.00 g, 24%) of the two as colorless needles, mp 111-113°; ir (potassium bromide): 1750 (CO₂C₂H₅), 1690 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.03 (t, J = 7 Hz, 6H, CH₃CH₂CH and CH₃CH₂CH), 1.24 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.79-2.10 (m, 6H, CH₂CH₂CH and CH₂CH₂CH), 2.60-2.92 (m, 4H, CH₂CH₂CH₂), 4.19 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 4.54 (t, J = 7 Hz, 2H, CH₃CH₂CHCO₂ and CH₃CH₂CHCO₂), 6.88 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 9.3 (q), 14.2 (q), 19.0 (t), 26.0 (t), 43.2 (t), 61.1 (t), 80.0 (d), 117.9 (d), 129.6 (s), 148.6 (s), 171.2 (s), 202.5 (s).

Anal. Calcd. for C₂₃H₃₀O₆: C, 63.58; H, 6.96. Found: C, 63.47; H, 6.91.

Diethyl 2,2'-(5,9-Dioxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1,4-diyloxy)-3,3'-dimethyl dibutyrate **4d**.

A mixture of **6** (1.00 g, 4.85 mmoles), ethyl 2-bromo-3-methylbutyrate (4.10 g, 19.6 mmoles), tripotassium phosphate (3.10 g, 14.6 mmoles), and dimethyl sulfoxide (10.0 ml) was heated at 60° for 6 hours with stirring. The mixture was extracted with benzene. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene(19)-acetone(1) to give **4d** (0.80 g, 35%) as a mixture (1:1 ratio) of *dl* and *meso* isomers, colorless oil. The ¹H nmr spectra of both isomers were almost the same but ¹³C nmr spectra were different in several absorptions. The asterisk shows different peaks; ir (neat): 1750 (CO₂C₂H₅), 1700 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.02 (d, J = 7 Hz, 6H, CH(CH₃)₂), 1.05 (d, J = 7 Hz, 6H, CH(CH₃)₂), 1.23 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.84-2.90 (m, 8H, CH₂CH₂CH₂, CHCHCO₂, and CHCHCO₂), 4.18 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 4.33 (d, J = 5 Hz, 2H, CHCHCO₂ and CHCHCO₂), 6.81 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 14.2 (q), 18.5 (q), 19.1 (t), 31.8 (d), 43.1 (t)*, 43.2 (t)*, 61.0 (t), 83.2 (d), 116.8 (d)*, 116.9 (d)*, 129.5 (s), 148.5 (s)*, 148.6 (s)*, 170.6 (s)*, 170.7 (s)*, 201.8 (s)*, 202.4 (s)*.

Diethyl 2,2'-(5,9-Dioxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1,4-diyloxy)-2,2'-diphenyldiacetate **4e**.

A mixture of **6** (1.00 g, 4.85 mmoles), ethyl 2-bromo-2-phenylacetate (4.70 g, 4.12 mmoles), tripotassium phosphate (3.10 g, 14.6 mmoles), and dioxane (10.0 ml) was stirred for 3.5 hours at room temperature. After removal of the tripotassium phosphate the filtrate was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene(19)-acetone(1) to give **4e** (1.30 g, 51%) as a mixture (1:1 ratio) of *dl* and *meso* isomers, colorless oil. The as-

terisk shows different peaks in the nmr spectra; ir (neat): 1750 ($\text{CO}_2\text{C}_2\text{H}_5$), 1710 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.06 (t, $J = 7$ Hz, 6H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.70-2.10 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.50-2.82 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 4.05 (q, $J = 7$ Hz, 4H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.58 (s, 2H, PhCHCO_2 and PhCHCO_2)*, 5.63 (s, 2H, PhCHCO_2 and PhCHCO_2)*, 6.86 (s, 2H, Ar-H)*, 6.93 (s, 2H, Ar-H)*, 7.16-7.56 (m, 10H, Ph-H₁₀); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 18.9 (t), 43.1 (t), 61.4 (t), 80.7 (d)*, 81.0 (d)*, 118.7 (d)*, 119.1 (d)*, 127.1 (d), 128.2 (d), 128.6 (d)*, 128.8 (d)*, 130.3 (s), 135.1 (s)*, 135.2 (s)*, 148.2 (s)*, 148.3 (s)*, 169.3 (s), 201.9 (s)*, 202.0 (s)*.

8,9-Dihydro-7H-2,5-dioxacyclohepta[jkl]-as-indacene 5a.

This compound was obtained as colorless needles from hexane, mp 88-89°; ^1H nmr (deuteriochloroform): δ 1.98-2.22 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.90-3.10 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.28 (s, 2H, Ar-H₂), 7.38 (s, 2H, furan-H₂); ^{13}C nmr (deuteriochloroform): δ 26.1 (t), 26.3 (t), 107.0 (d), 120.5 (s), 122.8 (s), 139.9 (d), 150.4 (s).

Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{O}_2$: C, 78.77; H, 5.09. Found: C, 78.50; H, 5.30.

1,6-Dimethyl-8,9-dihydro-7H-2,5-dioxacyclohepta[jkl]-as-indacene 5b.

Colorless needles from benzene-hexane were obtained, mp 142-144°; ^1H nmr (deuteriochloroform): δ 1.88-2.16 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.35 (s, 6H, CH_3 and CH_3), 2.70-2.96 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.10 (s, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 12.0 (q), 26.4 (t), 104.8 (d), 114.9 (s), 123.3 (s), 148.9 (s), 149.2 (s).

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2$: C, 79.62; H, 6.24. Found: C, 79.35; H, 6.35.

1,6-Diethyl-8,9-dihydro-7H-dioxacyclohepta[jkl]-as-indacene 5c.

Colorless plates from hexanes were obtained, mp 77-78°; ^1H nmr (deuteriochloroform): δ 1.28 (t, $J = 7$ Hz, 6H, CH_2CH_3 and CH_2CH_3), 1.88-2.16 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.71 (q, $J = 7$ Hz, 4H, CH_2CH_3 and CH_2CH_3), 2.78-2.90 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.12 (s, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 12.9 (q), 20.2 (t), 26.3 (t), 26.5 (t), 105.0 (d), 114.0 (s), 123.5 (s), 148.9 (s), 154.3 (s).

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.28; H, 7.13. Found: C, 80.10; H, 7.13.

1,6-Diisopropyl-8,9-dihydro-7H-2,5-dioxacyclohepta[jkl]-as-indacene 5d.

Colorless plates from hexane were obtained, mp 134-135°; ^1H nmr (deuteriochloroform): δ 1.34 (d, $J = 7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$ and $\text{CH}(\text{CH}_3)_2$), 1.90-2.22 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.86-3.29 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}(\text{CH}_3)_2$, and $\text{CH}(\text{CH}_3)_2$), 7.14 (s, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 21.5 (q), 26.5 (t), 26.7 (d), 27.2 (t), 105.0 (d), 112.9 (s), 123.6 (s), 148.7 (s), 157.5 (s).

Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_2$: C, 80.24; H, 8.51. Found: C, 80.02; H, 8.32.

1,6-Diphenyl-8,9-dihydro-7H-2,5-dioxacyclohepta[jkl]-as-indacene 5e.

Colorless needles from benzene were obtained, mp >230°; ^1H nmr (deuteriochloroform): δ 2.10-2.38 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.28-3.42 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.24-7.57 (m, 8H, Ar-H and Ph-H), 7.73-7.86 (m, 4H, Ar-H and Ph-H).

Anal. Calcd. for $\text{C}_{25}\text{H}_{18}\text{O}_2$: C, 85.69; H, 5.18. Found: C, 85.50; H, 5.41.

Ethyl 8,9-Dihydro-7H-2,5-dioxacyclohepta[jkl]-as-indacene-1-carboxylate 7.

Colorless plates from benzene-hexane were obtained, mp 112-113°; ir (potassium bromide): 1710 cm^{-1} ($\text{CO}_2\text{C}_2\text{H}_5$); ^1H nmr (deuteriochloroform): δ 1.45 (t, $J = 7$ Hz, 3H, CH_2CH_3), 2.02-2.29 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.96-3.13 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.28-3.50 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 4.45 (q, $J = 7$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.31 (d, $J = 9$ Hz, 1H, Ar-H), 7.46 (s, 1H, furan-H), 7.48 (d, $J = 9$ Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 14.5 (q), 25.4 (t), 26.0 (t), 28.1 (t), 61.0 (t), 107.5 (d), 111.2 (d), 120.8 (s), 122.9 (s), 123.7 (s), 130.1 (s), 140.2 (s), 140.8 (d), 150.2 (s), 150.5 (s), 160.3 (s).

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_4$: C, 71.10; H, 5.22. Found: C, 70.90; H, 5.46.

Diethyl 8,9-Dihydro-7H-2,5-dioxacyclohepta[jkl]-as-indacene-1,6-dicarboxylate 8.

Colorless plates from benzene-hexane were obtained, mp 155-156°; ir (potassium bromide): 1720 cm^{-1} ($\text{CO}_2\text{C}_2\text{H}_5$); ^1H nmr (deuteriochloroform): δ 1.45 (t, $J = 7$ Hz, 6H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.00-2.34 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.30-3.44 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 4.43 (q, $J = 7$ Hz, 4H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.42 (s, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 14.5 (q), 24.8 (t), 27.6 (t), 61.1 (t), 111.5 (d), 123.5 (s), 129.7 (s), 140.7 (s), 150.0 (s), 159.9 (s).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_6$: C, 66.66; H, 5.30. Found: C, 66.65; H, 5.42.

Ethyl 1,6-Dimethyl-7,8-dihydro-1H-2,5-dioxacyclohepta[jkl]-as-indacene-1-carboxylate 9.

Colorless needles from benzene-hexane were obtained, mp 118-119°; ir (potassium bromide): 1750 cm^{-1} ($\text{CO}_2\text{C}_2\text{H}_5$); ^1H nmr (deuteriochloroform): δ 1.26 (t, $J = 7$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.76 (s, 3H, CH_3CCO_2), 2.35 (s, 3H, furan- CH_3), 2.50-2.96 (m, 4H, CH_2CH_2), 4.22 (q, $J = 7$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.83 (t, $J = 6$ Hz, 1H, C=CH), 6.70 (d, $J = 9$ Hz, 1H, Ar-H), 7.11 (d, $J = 9$ Hz, 1H, Ar-H).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_4$: C, 72.46; H, 6.08. Found: C, 72.38; H, 5.92.

Diethyl 1,6-Dimethyl-6,8-dihydro-1H-2,5-dioxacyclohepta[jkl]-as-indacene-1,6-dicarboxylate 10.

Yellow needles from ethanol were obtained, 127-128°; ir (potassium bromide): 1730 cm^{-1} ($\text{CO}_2\text{C}_2\text{H}_5$); ^1H nmr (deuteriochloroform): δ 1.28 (t, $J = 7$ Hz, 6H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.66 (s, 6H, CH_3 and CH_3), 3.55 (t, $J = 4$ Hz, 2H, C=CH CH_2), 4.22 (q, $J = 7$ Hz, 4H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.18 (t, $J = 4$ Hz, 2H, C=CH CH_2 and C=CH CH_2), 6.55 (s, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 24.7 (q), 31.6 (t), 61.9 (t), 89.6 (s), 111.2 (d), 116.9 (d), 120.5 (s), 139.0 (s), 154.6 (s), 170.9 (s).

Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_6$: C, 68.09; H, 5.99. Found: C, 67.94; H, 6.01.

Diethyl 6a-Hydroxy-1,6-dimethyl-6,6a,7,8-tetrahydro-1H-2,5-dioxacyclohepta[jkl]-as-indacene-1,6-dicarboxylate 11b.

Colorless plates from benzene-hexane were obtained, mp 119-121°; ir (potassium bromide): 3475 (OH), 1740 cm^{-1} ($\text{CO}_2\text{C}_2\text{H}_5$); ^1H nmr (deuteriochloroform): δ 1.24 (t, $J = 7$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.32 (t, $J = 7$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.41 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.86-2.80 (m, 4H, CH_2CH_2), 2.84 (broad s, 1H, OH), 4.17 (q, $J = 7$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.30 (q, $J = 7$ Hz,

2H, CO₂CH₂CH₃), 5.90 (dd, J = 3 and 8 Hz, 1H, C=CH), 6.72 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 14.0 (q), 14.2 (q), 19.6 (q), 24.0 (t), 25.1 (q), 27.6 (t), 61.5 (t), 61.8 (t), 80.7 (s), 89.5 (s), 96.6 (s), 110.6 (d), 111.1 (d), 122.1 (s), 123.3 (d), 125.1 (s), 138.3 (s), 151.9 (s), 155.0 (s), 170.2 (s), 170.9 (s).

Anal. Calcd. for C₂₁H₂₄O₇: C, 64.93; H, 6.23. Found: C, 64.75; H, 6.20.

Diethyl 1,6-Diethyl-6a-hydroxy-6,6a,7,8-tetrahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **11c**.

Colorless plates from benzene-hexane were obtained, mp 133-134°; ir (potassium bromide): 3430 (OH), 1760 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 0.94 (t, J = 7 Hz, 6H, CH₂CH₃ and CH₂CH₃), 1.26 (t, J = 7 Hz, 3H, CO₂CH₂CH₃), 1.34 (t, J = 7 Hz, 3H, CO₂CH₂CH₃), 1.49-3.00 (m, 9H, CH₂CH₂, CH₂CH₃, CH₂CH₃, and OH), 4.20 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 4.33 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 5.92 (dd, J = 3 and 7 Hz, 1H, C=CH), 6.74 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 7.8 (q), 8.5 (q), 14.1 (q), 14.4 (q), 24.1 (t), 25.8 (t), 27.5 (t), 32.3 (t), 61.4 (t), 61.7 (t), 80.7 (s), 92.8 (s), 100.5 (s), 110.4 (d), 111.0 (d), 122.3 (s), 123.6 (d), 125.6 (s), 136.6 (s), 152.0 (s), 155.3 (s), 169.6 (s), 170.7 (s).

Anal. Calcd. for C₂₃H₂₈O₇: C, 66.33; H, 6.78. Found: C, 66.14; H, 6.90.

Diethyl 6a,9a-Dihydroxy-6,6a,7,8,9,9a-hexahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **12a**.

Colorless plates from benzene were obtained, mp 174-177°; ir (potassium bromide): 3500 (OH), 1760 (CO₂C₂H₅), 1735 cm⁻¹ (CO₂C₂H₅); ¹³C nmr (deuteriochloroform): δ 1.32 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.60-2.80 (m, 6H, CH₂CH₂CH₂), 3.46 (s, 2H, OH and OH), 4.26 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 4.73 (s, 2H, CHCO₂ and CHCO₂), 6.75 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 14.2 (q), 18.6 (t), 38.4 (t), 61.6 (t), 80.1 (s), 90.2 (d), 111.8 (d), 126.8 (s), 153.2 (s), 167.6 (s).

Anal. Calcd. for C₁₉H₂₂O₈: C, 60.31; H, 5.86. Found: C, 60.13; H, 5.91.

Diethyl 6a,9a-Dihydroxy-1,6-dimethyl-6,6a,7,8,9,9a-hexahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **12b**.

Colorless needles from benzene-acetone were obtained, mp 177-179°; ir (potassium bromide): 3500 (OH), 1755 (CO₂C₂H₅), 1740 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 1.31 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.44 (s, 6H, CH₃ and CH₃), 1.80-2.80 (m, 6H, CH₂CH₂CH₂), 3.21 (s, 2H, OH and OH), 4.23 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 6.76 (s, 2H, Ar-H₂); ¹³C nmr (deuteriochloroform): δ 14.2 (q), 17.9 (t), 20.4 (q), 34.5 (t), 61.7 (t), 82.3 (s), 95.5 (s), 112.3 (d), 126.6 (s), 152.1 (s), 170.4 (s).

Anal. Calcd. for C₂₁H₂₆O₈: C, 62.06; H, 6.45. Found: C, 61.88; H, 6.72.

Diethyl 1,6-Diethyl-6a,9a-dihydroxy-6,6a,7,8,9,9a-hexahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **12c**.

Colorless needles from benzene-acetone were obtained, mp 202-204°; ir (potassium bromide): 3540 (OH), 1760 (CO₂C₂H₅), 1730 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 0.93 (t, J = 7 Hz, 6H, CH₂CH₃ and CH₂CH₃), 1.31 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.42-2.90 (m, 10H, CH₂CH₂CH₂, CH₂CH₃, and CH₂CH₃), 3.24 (s, 2H, OH and OH), 4.20 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 4.23 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 6.76

(s, 2H, Ar-H); ¹³C nmr (deuteriochloroform): δ 8.6 (q), 14.2 (q), 17.8 (t), 26.5 (t), 34.2 (t), 61.5 (t), 82.1 (s), 99.4 (s), 111.9 (d), 126.9 (s), 152.2 (s), 169.9 (s).

Anal. Calcd. for C₂₃H₃₀O₈: C, 63.58; H, 6.96. Found: C, 63.53; H, 6.88.

Diethyl 6a,9a-Dihydroxy-1,6-diisopropyl-6,6a,7,8,9,9a-hexahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **12d**.

Colorless plates from benzene-hexane were obtained, mp 139-141°; ir (potassium bromide): 3500 (OH), 1760 (CO₂C₂H₅), 1730 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 0.56 (d, J = 7 Hz, 6H, CHCH₃ and CHCH₃), 0.98 (d, J = 7 Hz, 6H, CHCH₃ and CHCH₃), 1.31 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.60-2.95 (m, 10H, CH₂CH₂CH₂, CH(CH₃)₂, CH(CH₃)₂, OH, and OH), 4.22 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 6.75 (s, 2H, Ar-H₂).

Anal. Calcd. for C₂₅H₃₄O₈: C, 64.92; H, 7.41. Found: C, 65.15; H, 7.58.

Diethyl 6a,9a-Dihydroxy-1,6-diphenyl-6,6a,7,8,9,9a-hexahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **12e**.

Colorless needles from benzene-acetone were obtained, mp 228-230° dec; ir (potassium bromide): 3550 (OH), 3480 (OH), 1740 (CO₂C₂H₅), 1720 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 1.33 (t, J = 7 Hz, 6H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 1.50-2.70 (m, 6H, CH₂CH₂CH₂), 3.05 (broad s, 2H, OH and OH), 4.36 (q, J = 7 Hz, 4H, CO₂CH₂CH₃ and CO₂CH₂CH₃), 7.09 (s, 2H, Ar-H₂), 7.19-7.52 (m, 10H, Ph-H₁₀).

Anal. Calcd. for C₃₁H₃₀O₈: C, 70.17; H, 5.70. Found: C, 69.90; H, 5.95.

Diethyl 9a-Hydroxy-7,8,9,9a-tetrahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1,6-dicarboxylate **13**.

Colorless plates from benzene-acetone were obtained, mp 209-210°; ir (potassium bromide): 3430 (OH), 1740 (CO₂C₂H₅), 1710 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 1.38 (t, J = 7 Hz, 3H, CO₂CH₂CH₃), 1.42 (t, J = 7 Hz, 3H, CO₂CH₂CH₃), 1.80-3.84 (m, 7H, CH₂CH₂CH₂ and OH), 4.38 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 4.42 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 4.94 (s, 1H, CHCO₂), 7.03 (d, J = 9 Hz, 1H, Ar-H), 7.38 (d, J = 9 Hz, 1H, Ar-H).

Anal. Calcd. for C₁₉H₂₀O₇: C, 63.33; H, 5.59. Found: C, 63.60; H, 5.56.

Ethyl 9a-Hydroxy-1,6-dimethyl-7,8,9,9a-tetrahydro-1*H*-2,5-dioxacyclohepta[*ijkl*]-as-indacene-1-carboxylate **14**.

Colorless plates from benzene-hexane were obtained, mp 148-150°; ir (potassium bromide): 3550 (OH), 1740 cm⁻¹ (CO₂C₂H₅); ¹H nmr (deuteriochloroform): δ 1.36 (t, J = 7 Hz, 3H, CO₂CH₂CH₃), 1.48 (s, 3H, CH₃CCO₂), 1.70-3.16 (m, 7H, CH₂CH₂CH₂ and OH), 2.34 (s, 3H, furan-CH₃), 4.34 (q, J = 7 Hz, 2H, CO₂CH₂CH₃), 6.74 (d, J = 9 Hz, 1H, Ar-H), 7.18 (d, J = 9 Hz, 1H, Ar-H).

Anal. Calcd. for C₁₈H₂₀O₅: C, 68.34; H, 6.37. Found: C, 68.15; H, 6.55.

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REFERENCES AND NOTES

- [1] Part II. T. Horaguchi, H. Kobayashi, K. Miyazawa, E. Hasegawa, T. Shimizu, T. Suzuki, and K. Tanemura, *J. Heterocyclic Chem.*, **27**, 935 (1990).
- [2] Burgstahler and L. W. Worden, *Org. Synth.*, Coll. Vol. **5**, 251 (1973); F. M. Dean, P. Halewood, S. Mongholsuk, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 1250 (1953); W. B. Whalley, *ibid.*, 3229 (1951); P. C. Johnson and A. Robertson, *ibid.*, 2381 (1950).
- [3] H. Singh and R. S. Kapil, *J. Org. Chem.*, **24**, 2064 (1959); Ng. Ph. Buu-Hoi, G. Saint-Ruf, T. B. Loc and Ng. D. Xuong, *J. Chem. Soc.*, 2593 (1957); W. B. Whalley and G. Lloyd, *ibid.*, 3213 (1956); E. D. Elliot, *J. Am. Chem. Soc.*, **73**, 754 (1951).
- [4] G. N. Walker and R. T. Smith, *J. Org. Chem.*, **36**, 305 (1971); G. M. Brooke, W. K. R. Musgrave, and T. R. Thomas, *J. Chem. Soc. C*, 3596 (1971).
- [5] T. Horaguchi, H. Yagoh, K. Tanemura, and T. Suzuki, *J. Heterocyclic Chem.*, **23**, 657 (1986).
- [6] V. C. Farmer, N. F. Hayes, and R. H. Thomson, *J. Chem. Soc.*, 3600 (1956); E. A. Braude and F. Sondheimer, *ibid.*, 3754 (1955).
- [7] A. J. S. Sorrie and R. H. Thomson, *J. Chem. Soc.*, 2233 (1955).
- [8] T. Horaguchi, H. Narita, and T. Suzuki, *Bull. Chem. Soc. Japan*, **56**, 184 (1983).