ν_{CO} 1730 cm^{-1}; λ_{max} (in 95% ethanol) 228 mμ (log ϵ 4.59), 315 (3.98), 485 (4.08); nmr peaks in DMSO-d_6 at δ 2.0 (3 H, s), 7.2 (15 H, m), and 13.8 (1 H, s).

Anal. Calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.78; H, 5.00; N, 6.83.

Reaction of 5 with Aqueous Sodium Hydroxide in the Presence of β-Naphthol.—N-(*o*-Nitrophenylsulfonyl)-2-phenylacetamide (1.6 g, 0.005 mol) and β-naphthol (0.72 g, 0.005 mol) were mixed with 10% aqueous sodium hydroxide (30 ml) and heated on a steam bath for 14 hr. A gummy precipitate was present. After crystallization from ethanol and elution through a short column of alumina, 3-phenylindazole (0.66 g, 0.0034 mol, 68%), mp 116–118°, was obtained.

Acidification of the aqueous reaction solution precipitated β-naphthol (0.70 g, 0.0049 mol, 97%), mp 121–122° after purification by chromatography.

Reaction of *o*-Nitrophenylacetamide with Aqueous Sodium Hydroxide.—A mixture of *o*-nitrophenylacetamide (1.8 g, 0.010 mol) and 10% aqueous sodium hydroxide was heated on a steam bath for 7 hr. Acidification of the reaction mixture followed by recrystallization of the precipitate from ethanol–water gave *o*-nitrophenylacetic acid (1.0 g, 0.05 mol, 55%), mp 138–141°.

N-Methyl-N-(*o*-nitrophenylsulfonyl)-2-phenylacetamide (8).—N-Methyl-*o*-nitrobenzenesulfonamide (10.8 g, 0.050 mol) and phenylacetyl chloride (12.4 g, 0.080 mol) were heated together at 150–160° in an oil bath for 2 hr. Crushed ice was added to the reaction mixture with stirring and the precipitate was collected by filtration. Several recrystallizations from ethanol gave pure **8** (12.1 g, 0.036 mol, 72%): mp 126.5–128°; ν_{CO} 1700, ν_{NO_2} 1540 and 1355, ν_{SO_2} 1175 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.88; H, 4.22, N, 8.38. Found: C, 53.80; H, 4.17; N, 8.21.

Reaction of 8 with Aqueous Sodium Hydroxide.—A solution of **8** (1.67 g, 0.050 mol) in 10% aqueous sodium hydroxide (12.5 ml) was heated on a steam bath for 4.5 hr. The reaction mixture contained an oil which was dissolved in ether. The aqueous solution was extracted with ether. The combined ether solutions were washed with water, dried, and evaporated. The residue was chromatographed on silicic acid. N-Methyl-(*o*-nitrophenyl)phenylacetamide (**9**) was eluted with chloroform and recrystallized from ethanol (0.37 g, 1.4 mol, 88% based on unrecovered **8**): mp 142–144°; ν_{NH} 3250, ν_{CO} 1645, ν_{NO_2} 1525 and 1345 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.43, H, 5.39; N, 10.32.

Acidification of the aqueous reaction mixture gave unreacted **8** (1.15 g, 0.034 mol, 68% recovery).

Registry No.—**1**, 20512-89-4; **2**, 20512-90-7; **4**, 20512-91-8; **8**, 20512-92-9; **9**, 20512-93-0.

The Synthesis of (+)-, (−)-, and (±)-Dimethyl 3-Methyl-1-cyclopentene-1,2-dicarboxylates and the Corresponding Acids

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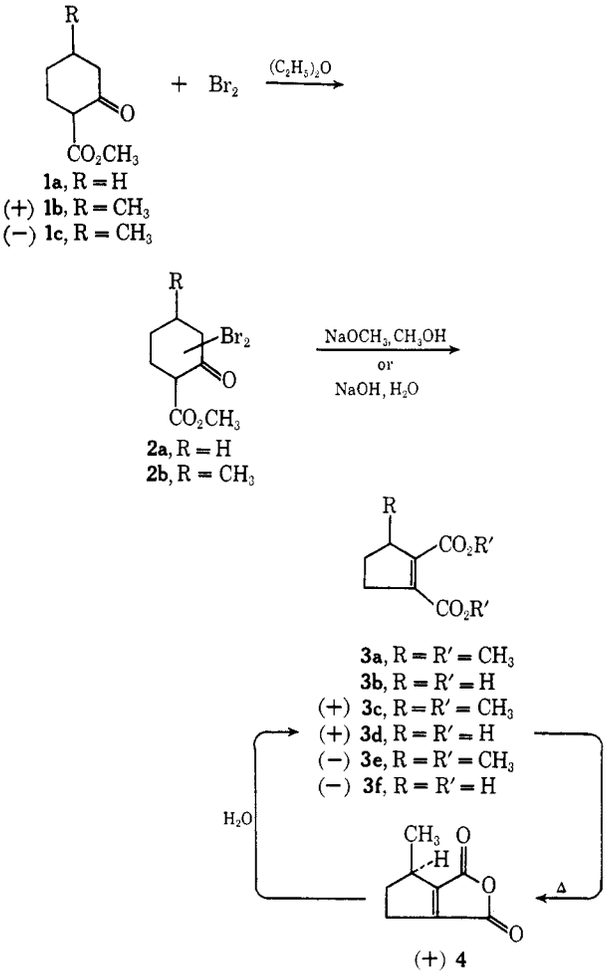
The synthesis of 1-cyclopentene-1,2-dicarboxylic acid and its dimethyl ester has been reported.[3] However, the reported synthesis of comparable esters with alkyl substitution at positions C-3 and C-4 are time consuming and multistep, and the over-all yields are low.[3c] We describe a convenient two-step general synthesis for esters or acids of these types. This reaction sequence, a Favorskii-type rearrangement of dibromo derivatives of β-keto esters, was first applied to 4,4-dibromo-2-methylacetoacetic acid.[4]

As shown in Scheme I, methyl 2-oxocyclohexanecarboxylate (**1a**), (+)-methyl 4-methyl-2-oxocyclohexanecarboxylate (**1b**), and (−)-methyl 4-methyl-2-oxocyclohexanecarboxylate (**1c**) on treatment with 2.2 molar equiv of bromine afforded the dibromides **2a** and **2b**.[5] These crude unidentified dibromides were then separately treated with a methanolic solution of sodium methoxide. Subsequent work-up provided the new esters (+)-dimethyl (3*R*)-methyl-1-cyclopentene-1,2-dicarboxylate (**3c**) and (−)-dimethyl (3*S*)-methyl-1-cyclopentene-1,2-dicarboxylate (**3e**). Hydrolysis of **2b**[5] yielded the new acids (+)-(3*R*)-methyl-1-cyclopentene-1,2-dicarboxylic acid (**3d**) and (−)-(3*S*)-methyl-1-cyclopentene-1,2-dicarboxylic acid (**3f**).

Dimethyl 1-cyclopentene-1,2-dicarboxylate (**3a**) and the acid **3b** were prepared and identified as described in the Experimental Section. The racemic forms of **3c**

SCHEME I



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(5) Structure **2b** is used to represent the dibromide from both (+) **1b** and (−) **1c**.

and **3d** are also known.[3c] The absolute configuration assignments of (+) **3c**, (+) **3d**, and (+) **4** as *R*[6] as well as (−) **3e** and (−) **3f** as *S*[6] are based on the use of (+)-(3*R*)-methylcyclohexanone[7a,b] and (−)-(3*S*)-methylcyclohexanone[7c] in the synthesis of (+) **1b** and (−) **1c**.

We found it convenient to use sodium methoxide in methanol to cause the Favorskii-type rearrangement since the product was thus directly available for distillation. However, aqueous sodium hydroxide may be used to cause the direct formation of the sodium salts of the dibasic acids **3b**, (+) **3d**, and (−) **3f**.

The nmr spectra of **3c** and/or **3e** show δ 1.15 (d, 3, J = 7 Hz), which is in agreement with a methyl-group split by a proton allylic to a double bond; 3.72 (s, 3) and 3.73 (s, 3) assigned to the two carboxymethyl groups; and a series of highly coupled resonances between 1.30 and 3.30 (m, 5) attributed to the protons of the cyclopentene ring. Their ir absorption (ester C=O) at 1720 cm^{-1} is comparable with that of maleic acid and not with the 1680-cm^{-1} value obtained for fumaric acid. Their ultraviolet spectra are in agreement with the reported value for the (±) form.[3c] The molecular ion peak at *m/e* 198 from their mass spectra lends additional support to the assigned structures.

The nmr spectrum of the acid **3d** in NaOD showed peaks compatible with the assigned structure. However, as expected, downfield shifts of about 29 Hz were observed and the methyl-group split appeared at δ 1.58 (d, 3, J = 7 Hz).

Experimental Section[8]

Dibromo Keto Ester 2a.—To a well-stirred solution of 25 g (0.16 mol) of methyl 2-oxocyclohexanecarboxylate (**1a**) and 200 ml of anhydrous ether at 0° was added dropwise 56 g (0.35 mol) of bromine. After the addition was complete, the solution was stirred for an additional hour at 0° and then added to 100 g of crushed ice and 100 ml of a saturated solution of sodium bicarbonate. The ether layer was separated and the aqueous layer was extracted with three additional 100-ml portions of ether. The ether layers were combined, dried ($MgSO_4$), and concentrated to 40 g (78%) of crude **2a**: nmr (neat) δ 3.80 (s, 3), 2.90 (m, 2), 2.40 (m, 2), and 1.80 (m, 2); ir (liquid film) 2950, 1730, 1650, 1620, 1440, 1360, 1340, 1240, 790, and 730 cm^{-1}. This crude material was used directly in the next step.

Dimethyl 1-Cyclopentene-1,2-dicarboxylate (3a).—To a well-stirred solution of sodium methoxide (12 g, 0.52 g-atom of sodium) in 200 ml of methanol was added dropwise at room temperature 40 g (0.127 mol) of **2a**. After the addition was complete, the solution was allowed to stir for 1 hr, poured into 200 ml of 5% hydrochloric acid solution, and extracted with five 100-ml portions of ether. The ether extracts were combined and washed with distilled water until neutral to pH paper, dried ($MgSO_4$), concentrated, and distilled, giving 19 g (81%) of dimethyl 1-cyclopentene-1,2-dicarboxylate (**3a**): bp 63° (0.4 mm); ir (liquid film) 2950, 1730, 1640, 1440, 1330, 1275, and 1200 cm^{-1}; nmr (CCl) δ 3.65 (s, 3), 3.64 (s, 3), 2.60 (t, 4, J = 6 Hz), 2.00 (q, 2, J = 7 Hz); mass spectrum (70 eV) molecular ion peak at *m/e* 184.[9] Hydrolysis of 450 mg of **3a** in 1 ml of 10% NaOH at room temperature yielded 210 mg (55%) of brown leaflets of 1-cyclopentene-1,2-dicarboxylic acid (**3b**), mp 150–160° and 176–177° after recrystallization from ethyl acetate (lit.[7a] mp 178–179°).

Dibromo Keto Ester 2b.—The procedure described for the preparation of **2a** was applied to 29 g (0.17 mol) of **1b**, which was dibrominated to yield 41.3 g (75%) of crude **2b**: ir (liquid film) 2950, 1730, 1660, 1620, 1440, 1360, 1260, 1250, 1220, 1160, 1100, 960, 810, 780, and 740 cm^{-1}.

(+)-Dimethyl (3*R*)-Methyl-1-cyclopentene-1,2-dicarboxylate (3c).—The procedure described for the preparation of **3a** was used to convert 41.3 g (0.126 mol) of **2b** into 22 g (88%) of **3c**: bp 45° (0.2 mm); $[\alpha]^{23}D$ +29.6° (*c* 1.2, CH_3OH); nmr (CCl_4) δ 3.73 (s, 3), 3.72 (s, 3), and 1.15 (d, 3, J = Hz); the remaining five protons were observed as complex resonances between 1.7 and 3.5; ir (liquid film) 2950, 1725, 1640, 1430, and 1260 cm^{-1}; uv max (CH_3OH) 223 mμ (log ϵ 4.33); mass spectrum 70 eV molecular ion *m/e* 198.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.39; H, 7.11.

(+)-(3*R*)-Methyl-1-cyclopentene-1,2-dicarboxylic Acid (3d).—To a well-stirred solution of 20 g (0.5 mol) of sodium hydroxide in 200 ml of distilled water at room temperature was added 41.3 g (0.126 mol) of **2b** prepared from (+) **1b**. After the addition was complete, the solution was allowed to stir for an additional hour and it was then added to 200 ml of a 5% solution of hydrochloric acid and extracted with five 100-ml portions of ether. The ether extracts were combined, dried ($MgSO_4$), and concentrated to 20 g (80%) of brown crystals, mp 105–125°. Recrystallization from petroleum ether (bp 60–68°) gave 14 g of colorless crystals of **3d**: mp 135–136°; nmr ($CDCl_3$) δ 8.75 (s, 2), 4.25 (m, 1), 3.60 (m, 2), and 1.30 (d, 3, J = 7 Hz); ir ($CHCl_3$) 3000, 1720, 1625, 1420, 1250, 1040, and 930 cm^{-1}; uv max (C_2H_5OH) 236 mμ (log ϵ 4.05); $[\alpha]^{24}D$ +12.1° (*c* 0.5, CH_3OH).

Anal. Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.38; H, 5.97.

(−)-Dimethyl (3*S*)-Methyl-1-cyclopentene-1,2-dicarboxylate (3e) and (−)-(3*S*)-Methyl-1-cyclopentene-1,2-dicarboxylic Acid (3f).—A 1.7-g sample of (−) 1c[7a,c] was converted into 1.06 g (53%) of (−) **3e**: bp 88–90° (0.1 mm); $[\alpha]D$ −28.7° (*c* 6.6, CH_3OH); molecular ion peak *m/e* 198. The mass, nmr, and ir spectra of (+) **3c** and (−) **3e** were essentially identical.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.40; H, 7.22.

An 0.2-g sample of (−) **3e** was treated with aqueous alkali as described for **3c** to give 0.11 g (64%) of (−) **3f**. Recrystallization of (−) **3f** from pentane afforded colorless crystals: mp 132–133°; $[\alpha]D$ −12.6° (*c* 1.0, CH_3OH). The nmr, ir, and uv spectra of (−) **3f** were essentially identical with those of (+) **3d**.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.51; H, 5.96.

(+)-(3*R*)-Methyl-1-cyclopentene-1,2-dicarboxylic Acid Anhydride (4).—A 0.28-g sample of crude **3d** was distilled at 180° (1 mm) to give 0.21 g (83%) of **4**: $[\alpha]^{23}D$ +17.4° (*c* 2.1 $CHCl_3$); ir (liquid film) 2945, 1840, 1770, 1650, 1450, 1325, 1265, 1105, 1075, 1030, 866, 729, and 718 cm^{-1}; nmr (CCl_4) δ 2.70 (m, 3), 2.20 (m, 2), and 1.25 (d, 3, J = 7 Hz). A sweep past δ 8.75 showed absence of absorption due to carboxyl proton.

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.45; H, 5.01.

Hydrolysis of **4** with warm water and recrystallization of the product from ethyl acetate gave **3d**, mp 135–136°.

Registry No.—**3a**, 13368-79-1; **3c**, 20512-95-2; **3d**, 20512-96-3; **3e**, 20512-97-4; **3f**, 20512-98-5; **4**, 20512-99-6.

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(8) Spectral data were obtained from Varian A-60, Beckman IR-5a, and Beckman DK-1 spectrometers. The nmr measurements are in δ 0 ppm from tetramethylsilane standard: m, multiplet; q, quartet; t, triplet; d, doublet; and s, singlet.

(9) This mass spectrum and others were obtained from a Consolidated Electrodynamics Corp. Model 21-103C spectrometer.