multiplet comprises five protons from the one phenyl ring. The less perturbed multiplet at δ 7.47 is assigned to the unencumbered phenyl group at C(4) [C(4′)].

The assignment of the $^{13}C$ spectrum relies heavily on the assignments of that for the *E* isomer **2**, in which extensive single-frequency, proton-decoupling experiments were possible.[2] Of the protonated carbon resonances, those at δ 122.8 and 129.9 were assigned to C(6) and C(5), respectively, in the same order as in **2**. Of the five most intense lines, that at δ 126.7 is assigned to the ortho carbons C(9), C(13) of the most sterically restricted phenyl group attached to C(7) and that at δ 127.8 to the ortho carbons C(15), C(19) of the unrestricted phenyl group at C(4).

Of the seven, low-intensity quaternary carbons, the three at δ 120.8, 130.7, and 138.2 are very weak and are therefore assigned to $C_3$, $C_1$, and $C_2$, respectively, on the basis of those in **2** and their distance from protons (assuming dipole–dipole relaxation to be dominant for these carbon atoms).

**Acknowledgment.** Financial assistance from the New Zealand Universities Grants Committee and the Australian Research Grants Committee is gratefully acknowledged.

**Registry No.** 1, 33253-76-8; (*Z*)-3, 65961-19-5.

**Supplementary Material Available:** Tables of atomic coordinates and thermal vibration parameters for nonhydrogen atoms and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

## Rearrangements of Allylic Acetates Catalyzed by Palladium(II): An Enantiospecific Synthesis of a Key Intermediate for the Preparation of 12-Hydroxyprostaglandins

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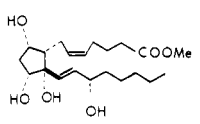
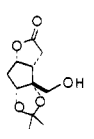
*Received May 19, 1981*

Our continued interest in prostaglandins possessing luteolytic properties has led us to develop an enantiospecific synthesis of 12-hydroxyprostaglandin $F_{2\alpha}$ methyl ester (**1**),

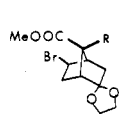



1

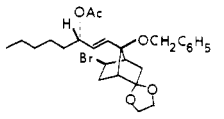



2

which we have previously shown in racemic form exhibits, when compared with natural $PGF_{2\alpha}$, comparable activity in terminating pregnancy in hamsters while displaying only minimal smooth muscle stimulating properties.[1] Since the original report describing the synthesis of (±)-**1** was published, which proceeded via the intermediacy of bicyclic lactone **2**,[1] Nelson and Scahill of the Upjohn Laboratories have detailed a synthesis of **2** in optically active form.[2] We describe here the efficient transformation of the known optically pure bromo ketal ester **3** (R = H)[3] into the enantiomerically pure bicyclo[2.2.1]heptane derivative **4**, which represents a viable intermediate along the pathway to **1**, employing the "conventional" bicyclo[2.2.1]heptane route to prostaglandins.

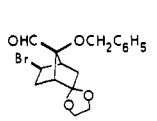



3

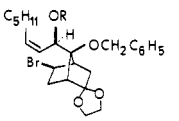



4

The conversion of **3** (R = H) into **4** was reduced to practice as a result of two completely stereocontrolled operations. The first centered around the observation that addition of 1-lithio-1-*cis*-heptene[4] to aldehyde **5**,[5] $[\alpha]^{25}_D$ −109.2° (*c* 2.04, $CHCl_3$), provided allylic alcohol **6** (R = H), $[\alpha]^{25}_D$ −58.5° (*c* 2.74, $CHCl_3$), in 86% isolated yield as the sole product. The exclusive formation of **6** (R = H) was not totally unexpected in view of prior experience with similar systems.[6a,b]

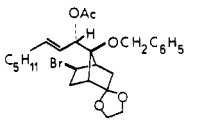



5




6

Taking advantage of the fact that catalytic amounts of palladium(II) salts will equilibrate allylic acetates with complete chirality transfer,[6a,c] we subjected the acetate **6** (R = Ac) derived from **6** (R = H) to rearrangement [$PdCl_2(CH_3CN)_2$ (0.04 equiv), THF, 24 h], giving rise (77%) to a single rearranged allylic acetate, **4**. Note that under the reaction conditions, the catalyst would be expected to set up an equilibrium between the desired allylic acetate **4** and the undesired *trans*-allylic acetate **7**. Despite this, one finds no trace of the allylic acetate **7**. The absence of **7** is reasonable in view of the conformational rigidity of the bicyclo[2.2.1]heptane ring system and the presence of the C(5) bromine atom; both factors act to drive the equilibrium between **4** and **7** in favor of **4** by minimizing steric congestion.




7

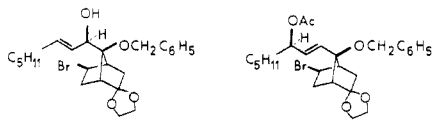
The configuration about the newly created chiral center was unambiguously established by employing a modification of a procedure recently introduced by Just and Oh.[7] The method takes advantage of the fact that (+)- and (−)-2-acetoxyheptanal react with *l*-ephedrine, giving rise to oxazolidines whose $R_f$ values on TLC analysis are characteristic of the absolute configuration about the carbon bearing the acetoxy function. Ozonolysis (10 min) of **4** (10 mg) in dry methylene chloride (0.3 mL) at 0 °C using 0.75 mL of a 0.04 M solution of ozone in methylene

(1) Grieco, P. A.; Yokoyama, Y.; Withers, G. P.; Okuniewicz, F. J.; Wang, C.-L. J. *J. Org. Chem.* **1978**, *43*, 4178.
(2) Nelson, N. A.; Scahill, T. A. *J. Org. Chem.* **1979**, *44*, 2790.
(3) Grieco, P. A.; Owens, W.; Wang, C.-L. J.; Williams, E.; Schillinger, W. J.; Hirotsu, K.; Clardy, J. *J. Med. Chem.* **1980**, *23*, 1072.
(4) Prepared from the corresponding 1-iodo-1-*cis*-heptene (Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.
(5) Aldehyde **5** was prepared via a four-step sequence: α-Hydroxylation of **3** (R = H) using the previously published procedure[1] gave rise to **3** (R = OH), $[\alpha]^{25}_D$ +1.7° (*c* 2.18, $CHCl_3$), which upon benzylation afforded **3** (R = $OCH_2C_6H_5$). Reduction of ester **3** (R = $OCH_2C_6H_5$) and subsequent Collins oxidation provided aldehyde **5** (see Experimental Section).
(6) (a) Grieco, P. A.; Takigawa, T.; Bongers, S. L.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 7587. (b) Majetich, G.; Grieco, P. A.; Bongers, S.; Erman, M. G.; Langs, D. A. *J. Org. Chem.* **1981**, *46*, 209. (c) Also see Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 5200. Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321.
(7) Just, G.; Oh, H. *Tetrahedron Lett.* **1980**, 3667.

0022-3263/81/1946-5005$01.25/0 

chloride followed by addition of dimethyl sulfide (10 μL) gave after 3 h a mixture of 2(S)-acetoxyheptanal and aldehyde **5** which upon treatment (30 min) with *l*-ephedrine (5 mg) in methylene chloride (0.5 mL) and reduction[8] ($NaBH_4$, EtOH) afforded two oxazolidines, $R_f$ 0.33 (major) and 0.18 (minor) [hexane–ethyl acetate, 5:1] [lit.[7] $R_f$ 0.33 (major), 0.18 (minor)]; both values are in accord with the *S* configuration for the isolated 2-acetoxyheptanal.

In a separate series of experiments, aldehyde **5** was condensed with 1-lithio-1-*trans*-heptene,[9] which afforded exclusively (95%) *trans*-allylic alcohol **8**. Acetylation [$Ac_2O$, Py, $CH_2Cl_2$, DMAP[10]] of **8** followed by rearrangement [$PdCl_2(CH_3CN)_2$ (0.04 equiv), THF, 24 h] provided (77%) as the only isolable product *trans*-allylic acetate **9**, $[\alpha]^{25}_D$ −30.6° (*c* 2.36, $CHCl_3$). Utilization of the above modification of Just's micromethod for determining the absolute configuration about the newly created chiral center at C(15) (prostaglandin numbering) confirmed the *R* configuration.[11]




8 9

## Experimental Section

Melting points were determined on a Fisher-Johns hot-stage melting-point apparatus. All melting points are uncorrected. Infrared (IR) spectra were determined on a Perkin-Elmer 298 grating infrared spectrometer and nuclear magnetic resonance (NMR) spectra were recorded at 220 MHz. Chemical shifts are reported in parts per million (δ) relative to $Me_4Si$ ($\delta_{Me_4Si}$ = 0.0 ppm) as an internal standard. Rotations were carried out at 25–28 °C on a Perkin-Elmer 241 polarimeter. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reactions were run under an atmosphere of argon. "Dry" solvents were dried immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride; dimethyl sulfoxide and pyridine were distilled from calcium hydride. Diethyl ether was distilled from sodium. Methylene chloride was passed through a column of alumina prior to use. Thin-layer chromatography (TLC) was carried out on Analtech (Uniplate) glass plates precoated with silica gel GF (250 μm).

**Methyl (−)-(1α,4α,5α,7*R**)-5-Bromo-7-(benzyloxy)spiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane]-7-carboxylate (3, R = $OCH_2C_6H_5$).** To a suspension of 217 mg (9.04 mmol) of sodium hydride (washed with heptane prior to use) in 30 mL of dry benzene containing 3 mL of dimethyl sulfoxide was added 1.85 g (6.03 mmol) of methyl (+)-(1α,4α,5α,7*R**)-5-bromo-7-hydroxyspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane]-7-carboxylate (**3**, R = OH).[1] After 1.5 h at 65 °C, 1.55 g (9.04 mmol) of benzyl bromide was added. Stirring at 65 °C was continued for 18 h. The reaction was quenched at room temperature with ice water and the product isolated by extraction with ether. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure left 2.40 g of crude material, which was chromatographed on 200 g of silica gel. Elution with hexane–ether (7:1) gave 2.15 g (90%) of pure crystalline **3** (R = $OCH_2C_6H_5$): mp 86–87 °C; $[\alpha]^{25}_D$ −30.5° (*c* 3.33, $CHCl_3$); IR ($CHCl_3$) 2990, 2950, 2880, 1726, 1495, 1450, 1430, 1387, 1325, 1312, 1280, 1265, 1245, 1200, 1170, 1145, 1105, 1080, 1060, 1040, 1020, 1005, 975, 945, 925, 885, 860, 836, 690 $cm^{-1}$; NMR (220 MHz) $CDCl_3$ δ 1.68 (d, 1 H, *J* = 14 Hz, C(3) endo proton), 2.43 (dt, 1 H, *J* = 14, 5 Hz), 2.6–2.9 (m, 4 H), 3.79 (s, 3 H, $OCH_3$), 3.8–4.1 (m, 5 H), 4.48 (ABq, 2 H, *J* = 12 Hz, $\Delta\nu_{AB}$ = 104.3 Hz, $OCH_2C_6H_5$), 7.3–7.5 (m, 5 H, $C_6H_5$). An analytical sample was prepared by recrystallization from hexane–ether, mp 87–88 °C.

Anal. Calcd for $C_{18}H_{21}BrO_5$: C, 54.42; H, 5.33. Found: C, 54.65; H, 5.57.

**(−)-(1α,4α,5α,7*R**)-5-Bromo-7-(benzyloxy)-7-formylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane] (5).** To a suspension of 432 mg (9.0 mmol) of lithium aluminum hydride in 100 mL of anhydrous ether cooled to 0 °C under an atmosphere of argon was added dropwise over 10 min 1.19 g (3.0 mmol) of **3** (R = $OCH_2C_6H_5$) in 20 mL of dry ether. After addition was complete, the temperature was raised to 25 °C, where stirring was continued for 6 h. The reaction was quenched by the addition of ice water. Usual workup provided 1.20 g of crude product. Chromatography on 200 g of silica gel using hexane–ether (2:1) afforded 1.06 g of (1α,4α,5α,7*R**)-5-bromo-7-(benzyloxy)spiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane]-7-methanol: $[\alpha]^{25}_D$ −12.8° (*c* 3.12, $CHCl_3$); IR 3560, 2990, 2950, 2880, 1490, 1461, 1450, 1430, 1400, 1375, 1325, 1310, 1230, 1140, 1115, 1085, 1050, 1015, 990, 970, 940, 930, 885, 860, 835, 690 $cm^{-1}$; NMR (220 MHz) $CDCl_3$ δ 1.61 (d, 1 H, *J* = 14 Hz), 2.04 (dt, 1 H, *J* = 14, 5 Hz), 2.18 (t, 1 H, *J* = 6 Hz, OH), 2.32 (d, 1 H, *J* = 5 Hz), 2.5–2.8 (m, 3 H), 3.7–4.0 (m, 4 H), 4.14 (dd, 1 H, *J* = 9, 6 Hz, CHBr), 4.27 (d, 2 H, *J* = 6 Hz, $CH_2OH$), 4.57 (ABq, 2 H, *J* = 11 Hz, $\Delta\nu_{AB}$ = 38.4 Hz, $CH_2C_6H_5$), 7.3–7.6 (m, 5 H).

To a solution of 2.71 g (27.1 mmol) of chromium trioxide in 100 mL of dry methylene chloride cooled to 0 °C under an atmosphere of argon was added 4.39 mL (54.2 mmol) of dry pyridine. After 30 min at 0 °C, 25 g of Celite was added and the temperature was raised to 25 °C. After an additional 30 min, 1.00 g (2.71 mmol) of (−)-(1α,4α,5α,7*R**)-5-bromo-7-(benzyloxy)spiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane]-7-methanol in 50 mL of methylene chloride was added dropwise over 10 min. The reaction was quenched, 20 min after addition was complete, with 15.3 g of sodium hydrogen sulfate. The reaction was diluted with 100 mL of ether, and the contents of the flask were filtered through a pad of Celite. Removal of the solvent in vacuo provided 1.30 g of a residue, which was chromatographed on 200 g of silica gel. Elution with hexane–ether (4:1) provided 941 mg (95%) of pure aldehyde **5**: mp 83–84 °C; $[\alpha]^{25}_D$ −109.2° (*c* 2.04, $CHCl_3$); IR ($CHCl_3$) 3020, 3000, 2980, 2940, 2880, 2815, 2715, 1715, 1490, 1450, 1425, 1380, 1322, 1310, 1275, 1250, 1220, 1185, 1141, 1105, 1080, 1060, 1048, 1010, 990, 970, 940, 915, 904, 885, 865, 690 $cm^{-1}$; NMR (220 MHz) $CDCl_3$ δ 1.73 (d, 1 H, *J* = 14 Hz), 2.27 (dt, 1 H, *J* = 14, 5 Hz), 2.6–3.0 (m, 3 H), 3.86 (m, 4 H), 4.07 (dd, 1 H, J = 10, 4 Hz, CHBr), 4.41 (AB q, 2 H, *J* = 11 Hz, $\Delta\nu_{AB}$ = 110.4 Hz), 7.39 (m, 5 H), 9.82 (s, 1 H, CHO).

Anal. Calcd for $C_{17}H_{19}BrO_4$: C, 55.60; H, 5.21. Found: C, 55.31; H, 5.07.

**(−)-[1α,4α,5α,7*R**(*Z*)]-5-Bromo-7-(benzyloxy)spiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolan]-7-yl-1(*R**)-hydroxy-2-octene (6, R = H).** A solution of 368 mg (1.64 mmol) of 1-iodo-1-*cis*-heptene[4] in 4.0 mL of heptane cooled to −78 °C under an atmosphere of argon was treated at −78 °C with 690 μL (1.64 mmol) of a 2.38 M solution of *n*-butyllithium in hexane. After 30 min, 201 mg (0.548 mmol) of aldehyde **5** in 5.0 mL of dry tetrahydrofuran was added. After 1 h, the reaction mixture was warmed to 0 °C and was quenched with a saturated aqueous solution of ammonium chloride. The product was isolated by extraction with ether (3 × 50 mL). The combined ether extracts were washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure left 260 mg of a residue, which was chromatographed on 40 g of silica gel. Elution with hexane–ethyl acetate (10:1) provided 220 mg (86%) of pure **6** (R = H) as a colorless oil: $[\alpha]^{25}_D$ −58.5° (*c* 2.74, $CHCl_3$); IR ($CHCl_3$) 3560, 2990, 2955, 2930, 2870, 2850, 1495, 1450, 1430, 1370, 1340, 1320, 1250, 1180, 1125, 1100, 1055, 1010, 1000, 965, 950, 940, 920, 890, 860, 690 $cm^{-1}$; NMR (220 MHz) $CCl_4$ δ 0.89 (t, 3 H, *J* = 7 Hz), 1.32 (m, 6 H), 1.50 (d, 1 H, *J* = 14 Hz), 1.9–2.3 (m, 5 H), 2.36 (dd, 1 H, *J* = 14 Hz, 5 Hz), 2.68 (dd, 1 H, *J* = 14 Hz, 8 Hz), 2.86 (d, 1 H, *J* = 5 Hz), 3.6–4.0 (m, 4 H), 4.16 (dd, 1 H, *J* = 10, 5 Hz, CHBr), 4.80 (ABq, 2 H, *J* = 12 Hz, $\Delta\nu_{AB}$

(8) Aldehyde **5**, one of the products obtained upon ozonolysis of **4**, does not react with *l*-ephedrine due to steric reasons. As a consequence the $R_f$ value for **5** prevents rigorous analysis of the newly formed oxazolidines present. Reduction of **5** prior to workup removes the complications stemming from **5**, thus facilitating TLC analysis.

(9) Zwiefel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

(10) Hofle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 568.

(11) The oxazolidines obtained possessed $R_f$ values of 0.44 (major) and 0.23 (minor); both values are in complete agreement with the *R* configuration for the isolated 2-acetoxyheptanal.

= 124.4 Hz), 5.20 (dd, 1 H, $J$ = 10, 3 Hz, CHOH), 5.52 (dt, 1 H, $J$ = 10, 7 Hz, $CH_2CH$=CH), 5.80 (t, 1 H, $J$ = 10 Hz, CH=CHCHOH), 7.1-7.5 (m, 5 H).

**(-)-[1α,4α,5α,7R*(E)]-5-Bromo-7-(benzyloxy)spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolan]-7-yl-3(S*)-acetoxy-1-octene (4).** To a solution of 220 mg (0.473 mmol) of alcohol **6** (R = H) in 5.0 mL of dry methylene chloride containing 1.0 mL of acetic anhydride and 0.5 mL of pyridine was added a catalytic amount of 4-(dimethylamino)pyridine. After 24 h, the reaction mixture was diluted with 50 mL of ether and was washed successively with copper sulfate solution, water, sodium bicarbonate solution, and brine. The organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent in vacuo left 210 mg of residue, which was purified on 40 g of silica gel. Elution with hexane-ethyl acetate (15:1) gave 196 mg (82%) of pure acetate **6** (R = Ac) as a colorless oil: $[\alpha]^{25}_D$ +2.60 ($c$ 3.38, $CHCl_3$); IR ($CHCl_3$) 2990, 2950, 2920, 2870, 1735, 1490, 1460, 1450, 1430, 1365, 1320, 1310, 1235, 1204, 1130, 1090, 1050, 1012, 1000, 995, 940, 910, 890, 860, 690 $cm^{-1}$; NMR (220 MHz) $CCl_4$ δ 0.91 (br t, 3 H, $J$ = 7 Hz), 1.36 (m, 6 H), 1.55 (d, 1 H, $J$ = 14 Hz), 1.91 (br s, 1 H), 2.00 (m, 2 H), 2.03 (s, 3 H), 2.32 (dd, 1 H, $J$ = 14, 5 Hz), 2.41 (m, 1 H), 2.70 (dd, 1 H, $J$ = 15, 9 Hz), 2.90 (m, 1 H), 3.6-4.0 (m, 4 H), 4.09 (dd, 1 H, $J$ = 9, 4 Hz, CHBr), 4.78 (ABq, 2 H, $J$ = 12 Hz, $\Delta\nu_{AB}$ = 106.3 Hz), 5.57 (m, 2 H, CH=CH), 6.04 (d, 1 H, 8 Hz, CHOAc), 7.1-7.5 (m, 5 H).

To a solution of 190 mg (0.375 mmol) of bromo acetate **6** (R = Ac) in 5.0 mL of tetrahydrofuran was added 4.0 mg of bis(acetonitrile)palladium(II) chloride. After 24 h the reaction was diluted with 20 mL of ether and was washed with brine. The organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent in vacuo left 200 mg of a residue, which was chromatographed on 40 g of silica gel. Elution with hexane-ethyl acetate (30:1) gave 146 mg (77%) of rearranged acetate **4** as a pure crystalline compound: mp 83.5-84.5 °C; $[\alpha]^{25}_D$ -80.7° ($c$ 2.14, $CHCl_3$); IR ($CHCl_3$) 3000, 2950, 2925, 2870, 2855, 1728, 1605, 1495, 1465, 1450, 1440, 1430, 1370, 1330, 1240, 1205, 1140, 1115, 1095, 1055, 1015, 975, 945, 925, 890, 865, 835, 692 $cm^{-1}$; NMR (220 MHz) $CCl_4$ δ 0.87 (t, 3 H, $J$ = 7 Hz), 1.30 (m, 6 H), 1.50 (d, 1 H, $J$ = 14 Hz), 1.64 (m, 2 H), 1.93 (s, 3 H), 2.08 (dt, 1 H, $J$ = 14, 5 Hz), 2.33 (d, 1 H, $J$ = 5 Hz), 2.44 (d, 1 H, $J$ = 5 Hz), 2.64 (m, 2 H), 3.7-4.0 (m, 5 H, $OCH_2CH_2O$, CHBr), 4.30 (ABq, 2 H, $J$ = 12 Hz, $\Delta\nu_{AB}$ = 25.3 Hz), 5.23 (q, 1 H, $J$ = 7 Hz, CHOAc), 5.70 (dd, 1 H, $J$ = 16, 7 Hz, CH(OAc)CH=CH), 6.01 (d, 1 H, $J$ = 16 Hz, CH(OAc)CH=CH), 7.24 (m, 5 H).

Anal. Calcd for $C_{26}H_{35}BrO_5$: C, 61.54; H, 6.95. Found: C, 61.65; H, 7.04.

**Acknowledgment.** Generous support for this work from the National Institute of Child Health and Human Development, National Institutes of Health (Grant HD 14646), and G. D. Searle and Co. is gratefully acknowledged.

**Registry No. 3** (R = H), 79120-26-6; **3** (R = $OCH_2C_6H_5$), 79069-64-0; **4**, 79069-65-1; **5**, 79069-66-2; **6** (R = H), 79069-67-3; **6** (R = Ac), 79069-68-4; (-)-(1α,4α,5α,7R*)-5-bromo-7-(benzyloxy)spiro[bicyclo-[2.2.1]heptane-2,2'-[1,3]dioxolane]-7-methanol, 79069-69-5; 1-iodo-1-*cis*-heptene, 63318-29-6; $PdCl_2(CH_3CN)_2$, 14592-56-4.

## Isomeric Bicyclo[3.2.1]octane-6,8-diones: Nuclear Magnetic Resonance as a Probe for Stereochemical Distinction

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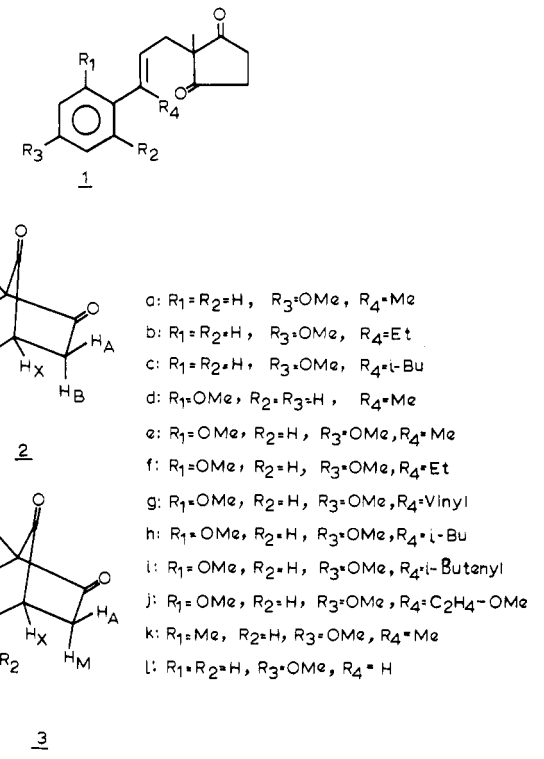
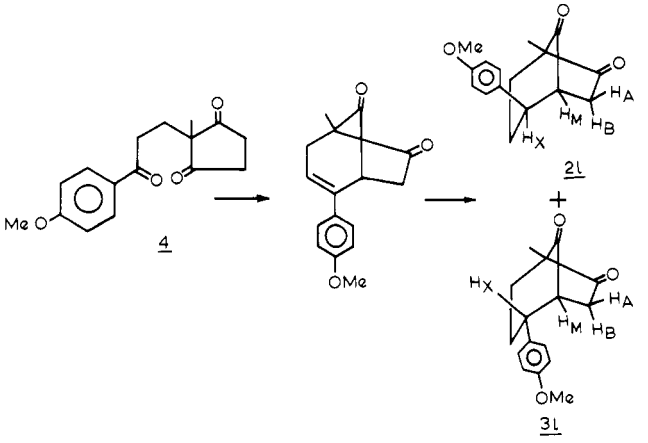
*Received May 22, 1981*

We have shown[1] earlier that the cyclization of diketones of the type **1** using hydrogen chloride in methanol gives

Chart I




Scheme I




isomeric bicyclo[3.2.1]octane-6,8-diones **2** and **3** (Chart I). These isomeric diones exhibit characteristic line patterns for the oxomethylene and the bridgehead protons in their $^1H$ NMR spectra (see Table I): pattern A (ABX),[2] $\delta_A$, $\delta_B$ 2.3-2.8 (m), $\delta_X$ 3.1-4.0 (m); pattern B (AMX), $\delta_A$ 2.4-2.7 (q, $J_{AX} \approx 8.0$ Hz, $J_{AM} \approx 20.0$ Hz), $\delta_M$ 2.8-3.0 (d, $J_{AM} \approx 20.0$ Hz), $\delta_X$ 3.3-4.1 (d, $J_{AX} \approx 8.0$ Hz). The isomers which exhibited pattern A were assigned the *exo*-2-aryl-*endo*-2-alkyl configuration (**2**) and those isomers which exhibited pattern B were assigned the *endo*-2-aryl-*exo*-2-alkyl configuration (**3**). These assignments were based on the expectation that the aryl group in the endo position (as in **3**) would deshield the *endo*-oxomethylene proton and thus lead to a larger chemical shift difference between *exo*- and *endo*-oxomethylene protons in this isomer. Similar de-

(1) T. R. Kasturi, S. Madhava Reddy, R. Ramachandra, and E. M. Abraham, *Indian J. Chem., Sect. B.*, **19B**, 433 (1980); T. R. Kasturi and S. Madhava Reddy, *ibid.*, **20B**, 64 (1981).

(2) Spectral analysis was carried out by using the LAOCN3 computer program (A. A. Bothner-By and S. Castelleno in "Computer Programs in Chemistry", Vol. 1, D. F. Detar, Ed., W. A. Benjamin, New York, 1968, p 10).

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