at 3.73 (4 H, H_C), an AB quartet at 5.46 (4 H, J = 15 Hz, $-CH_2S-$) and at 6.05 (4 H, J = 15 Hz, $-CH_2S-$); mass spectrum m/e 372.100 (calcd for $C_{24}H_{20}S_2$, 372.101).

Anal. Calcd for $C_{24}H_{20}S_2$: C, 77.40; H, 5.41. Found: C, 77.31; H, 5.27.

Benzyne–Stevens Rearrangement of 4 and 5. To a boiling solution of 74 mg of **5** and 210 mg of isoamyl nitrite in 30 ml of 1,2-dichloroethane under a nitrogen atmosphere there was added dropwise a solution of 68 mg of anthranilic acid in 10 ml of 1,2-dichloroethane. The addition required 1.5 h and the resulting reaction mixture was boiled under reflux for an additional 15 min. After concentration of the reaction mixture under reduced pressure, the residue was taken up in carbon tetrachloride and transferred to a silica gel column. Elution with benzene gave 60 mg (58%) of a pale yellow oil: mass spectrum m/e 524 (calcd for $C_{36}H_{28}S_2$, 524); NMR spectrum ($CDCl_3$) showing complex multiplets at τ 1.0, 2.0–3.6, 4.0–4.6, and 5.0–7.0, suggesting the presence of a mixture of **6** and **7**.

Similarly, when 19 mg of pure **4** was treated in an analogous way, there was isolated 17 mg (64%) of a pale yellow oil showing a parent molecular ion at m/e 524 and an essentially identical NMR spectrum as above.

Raney Nickel Desulfurization of the Benzyne–Stevens Rearrangement Products. A solution of 60 mg of the yellow oil (mixture of **6** and **7**) from the benzyne–Stevens rearrangement of pure **5** and 1 g of Raney nickel catalyst in 30 ml of absolute ethanol containing enough benzene for solubility of the organic constituents was boiled under reflux for 20 h. After removal of the catalyst and solvent, the residue was chromatographed over silica gel using a 1:2 mixture of carbon tetrachloride–hexane for elution. The first fraction of eluate gave 15 mg (41%) of the pure anti isomer **3**: mp 298–301 °C;[2] NMR ($CDCl_3$) a doublet of doublets at τ 2.26 (4 H, J = 6.0, J' = 3.0 Hz, H_A), a doublet of doublets at 2.59 (4 H, J = 6.0, J' = 3.0 Hz, H_B), a singlet at 4.23 (4 H, H_C), and an A_2B_2 multiplet at 6.1–7.2 (8 H, $-CH_2-$).

From the second fraction of eluate there was isolated 6 mg (16%) of white crystals of the pure syn isomer **1**: mp 242–245 °C;[3] NMR ($CDCl_3$) a doublet of doublets at τ 2.51 (4 H, J = 6.0, J' = 3.0 Hz, H_A), a doublet of doublets at 3.15 (4 H, J = 6.0, J' = 3.0 Hz, H_B), a singlet at 3.28 (4 H, H_C), and an A_2B_2 multiplet at 6.0–6.8 (8 H, $-CH_2-$).

Similarly, when 17 mg of the benzyne–Stevens rearrangement product from the pure syn isomer **4** was subjected to Raney nickel desulfurization, the products were the anti isomer **3** in 40% yield and the syn isomer **1** in 15% yield.

Syn and Anti Isomers of [2.2](1,4)Naphthalenophane-1,13-diene, 8 and 9. A solution of 59.5 mg of the benzyne–Stevens rearrangement product from **5** and 40 mg of *m*-chloroperbenzoic acid (85%) in 10 ml of chloroform was allowed to stand at room temperature overnight under a nitrogen atmosphere. The chloroform solution was washed successively with aqueous sodium bicarbonate and water, dried, and concentrated to give the corresponding bis sulfoxide as 63 mg (100%) of a pale yellow oil. This oil was pyrolyzed directly using a gradient sublimator at 300 °C and under 0.02 mm pressure. The mixture, which collected on the cold finger, was chromatographed over silica gel using a 1:2 mixture of carbon tetrachloride–hexane for elution. The first fraction of eluate gave 1.3 mg (4%) of the pure anti isomer **9** as white crystals: mp 252 °C dec; NMR ($CDCl_3$) a doublet of doublets at τ 2.37 (4 H, J = 6.0, J' = 3.0 Hz, H_A), a singlet at 2.55 (4 H, $-CH{=}CH-$), a doublet of doublets at 2.63 (4 H, J = 6.0, J' = 3.0 Hz, H_B), and a singlet at 4.26 (4 H, H_C).

Anal. Calcd for $C_{24}H_{16}$: mol wt, 304.125. Found (high-resolution mass spectrum): mol wt, 304.124.

The second fraction of eluate gave 0.2 mg (0.6%) of white crystals: mp 200 °C dec; NMR ($CDCl_3$) a singlet at τ 2.36 (4 H, $-CH{=}CH-$), a doublet of doublets at 2.72 (4 H, J = 6.0, J' = 3.0 Hz, H_A), a doublet of doublets at 3.23 (4 H, J = 6.0, J' = 3.0 Hz, H_B), and a singlet at 3.28 (4 H, H_C).

Anal. Calcd for $C_{24}H_{16}$: mol wt, 304.125. Found (high-resolution mass spectrum): mol wt, 304.125.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

Registry No.—**1**, 23284-44-3; **3**, 14724-91-5; **4**, 61158-76-7; **5**, 61216-66-8; **6**, 61158-81-4; **6** sulfoxide, 61247-61-8; **7**, 61216-68-0; **7** sulfoxide, 61158-82-5; **8**, 61158-77-8; **9**, 61216-67-9; 1,4-bis(bromomethyl)naphthalene, 58791-49-4; 1,4-bis(mercaptomethyl)-naphthalene, 59045-58-8; anthranilic acid, 118-92-3.

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Highly Stereoselective Synthesis of 9-*epi*-Prostaglandin $F_{2\alpha}$ and 11-*epi*-prostaglandin $F_{2\alpha}$ by the Aluminum Hydride Reduction of Prostaglandin E_2 and 11-*epi*-Prostaglandin E_2 Derivatives[1]

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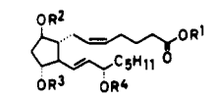
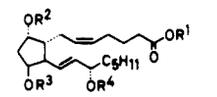
In connection with another study in progress in these laboratories, we required substantial quantities of 9-*epi*-prostaglandin $F_{2\alpha}$ ($PGF_{2\beta}$) (**1a**) and 11-*epi*-prostaglandin $F_{2\alpha}$ (**2a**). $PGF_{2\beta}$) or derivatives thereof) has been obtained as one component of the mixtures formed on the sodium borohydride reduction[2-5] of PGE_2 (**3a**) (or analogues), or the aluminum amalgam[5,6] reduction of the mixed 10,11-α- and -β-epoxides of PGA_2 (or derivatives). Analogous procedures[5,6] have been utilized to prepare 11-*epi*-$PGF_{2\alpha}$, but the efficiency of these processes is very low (see Table I, for example). Weinshenker et al.[7] have described a synthesis of this compound (**2a**) the



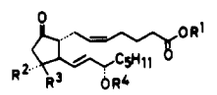
1

a) R^1, R^2, R^3, R^4 = H
b) R^1 = CH_3; R^2, R^3 = H; R^4 = CH_3CO
c) R^1 = CH_3; R^2, R^3, R^4 = H
d) R^1 = CH_3; R^2 = H; R^3, R^4 = THP



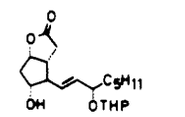
2

a) R^1, R^2, R^3, R^4 = H
b) R^1 = CH_3; R^2, R^3 = H; R^4 = CH_3CO
c) R^1 = CH_3; R^2, R^3, R^4 = H

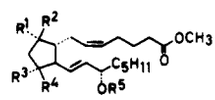


3

a) R^1, R^3, R^4 = H; R^2 = OH
b) R^1, R^2, R^4 = H; R^3 = OH
c) R^1 = CH_3; R^2 = OH; R^3 = H; R^4 = CH_3CO
d) R^1 = CH_3; R^2 = H; R^3 = OH; R^4 = CH_3CO
e) R^1 = CH_3; R^2 = OTHP; R^3 = H; R^4 = THP
f) R^1, R^3, R^4 = H; R^2 = $OSi(CH_3)_3$
g) R^1 = CH_3; R^2 = H; R^3 = $OSi(CH_3)_3$; R^4 = CH_3CO



4



5

a) R^1, R^3 = OH; R^2, R^4 = H; R^5 = CH_3CO
b) R^1, R^3 = H; R^2, R^4 = OH; R^5 = H or CH_3CO
c) R^1 = OH; R^2, R^4 = H; R^3 = OTHP; R^5 = THP

crucial aspect of which involved the nucleophilic inversion (tetraethylammonium formate on the tosylate) of the prostaglandin intermediate[8] **4**. Very recently, Corey and coworkers[9] have shown that both **1a** and **2a** were readily available by the stereospecific inversion of suitably protected 9- and 11-tosylates of $PGF_{2\alpha}$ with superoxide ion. This process, though useful, requires large amounts of the costly reagent 18-crown-6 to solubilize the potassium superoxide.

Table I. Reduction of PGE_2 and 11-*epi*-PGE_2 Derivatives

Registry no.	Substrate	Reducing agent	Group at C-11	Stereochemistry of reduction at C-9		Ref
				α	β	
363-24-6	PGE_2 (**3a**)	$NaBH_4$	α-OH	42	58	5
38310-90-6	11-*epi*-PGE_2 (**3b**)	$NaBH_4$	β-OH	21	79[a]	This work
37785-76-5	**3c**	AlH_3	α-OH	6	94[a]	This work
37785-77-6	**3d**	AlH_3	β-OH	100	0[a]	This work
54984-20-2	**3e**	AlH_3	α-THPO	40	60[a]	This work
61158-79-0	**3f**	$NaBH_4$	α-$(CH_3)_3SiO$	85	15	5
61218-48-2	**3g**	$NaBH_4$	β-$(CH_3)_3SiO$	0	100[a]	This work

[a] Ratio of isolated products.

Both PGE_2 and 11-*epi*-PGE_2 (**3b**) are easily prepared[5,6] from the corresponding 10,11-epoxides which in turn can be produced with a considerable degree of stereoselectivity from PGA_2.[10,11] It occurred to us that the transformation of **3a** and **3b** into **1a** and **2a** might be possible if a way could be devised to induce the hydroxyl moiety at C-11 to direct an intramolecular delivery[12] of hydride ion to the carbonyl group at C-9 without affecting other reducible groups in the substrate. For various reasons,[13] it was considered that aluminum hydride[14] would meet these requirements, and therefore an equimolar amount of Alane (aluminum hydride stabilized with triethylamine)[15] in benzene was added to a solution of PGE_2 methyl ester 15-acetate (**3c**) in tetrahydrofuran at −78 °C. Workup of the reaction after 15 min and separation of the mixture thus obtained by preparative thin layer chromatography (TLC) gave the starting material and three products **5a, 1b,** and **1c,** identified by direct comparison with authentic specimens, in a ratio of 20:4.5:26:49.5, respectively. Reduction from the α side had thus occurred with a selectivity greater than 94%! Reduction of 11-*epi*-PGE_2 methyl ester acetate (**3d**) in the same way gave the starting material, **2b,** and **2c** in a ratio of 15:54:31. No 9β,11β alcohol **5b** was formed and therefore hydride was introduced stereospecifically from the β face of the molecule. That a free hydroxyl group at C-11 was vital for the above stereochemical control was evident from the reduction of PGE_2 methyl ester bis(tetrahydropyranyl ether) (**3e**) in which case a 60:40 mixture of **1d** and **5c** was formed. This ratio was almost identical with that which has been reported[5] (see Table I) for the sodium borohydride reduction of PGE_2, but greatly different (15:85) from that which was obtained from the sodium borohydride reduction of the 11-trimethylsilyl ethers of PGE_2 derivatives.[5] Inasmuch as a bulky substituent at C-11 is known[5,16,17] to cause predominant or exclusive reduction with sodium borohydride to occur from the side opposite to this group (i.e., to give the cis-9,11 stereochemistry), the high proportion of the trans product formed in the reduction of **3e** with Alane is probably a reflection of a substantial intramolecular delivery of hydride even in the absence of a free hydroxyl group at C-11.

The alkaline hydrolysis of **1b, 1c, 2b,** and **2c** could be accomplished in yields exceeding 90%; thus $PGF_{2\beta}$ and 11-*epi*-$PGF_{2\alpha}$ were obtained in 76 and 86% overall yields (based on starting material consumed) from **3a** and **3b,** respectively.

The results described herein have a number of interesting and important implications of a mechanistic and synthetic nature.

Experimental Section

The melting points were determined in a Mel-Temp melting point apparatus and are not corrected. The rotations were measured with a Perkin-Elmer Model 141 polarimeter. The infrared spectra were recorded with a Perkin-Elmer Model 237 grating infrared spectrophotometer. The NMR spectra were obtained with a Varian T-60 spectrometer.

Aluminum Hydride Reduction of PGE_2 Methyl Ester 15-Acetate (3c). A solution of compound **3c** (0.500 g, 1.22 mmol) in anhydrous tetrahydrofuran (7.5 ml) was cooled to −70 °C in an atmosphere of argon. A 0.75 M solution (1.62 ml, 1.21 mmol) of Alane in benzene was mixed with anhydrous tetrahydrofuran (10.4 ml) and then added slowly with stirring, at −70 °C, to the solution of **3c.** Fifteen minutes after the addition was completed, water (5 ml) and 6 N hydrochloric acid (5 ml) were added at −70 °C. The product was extracted with ethyl acetate, and the extract was washed successively with saturated sodium bicarbonate and saturated sodium chloride solutions, and then dried over magnesium sulfate. The solvent was removed in vacuo and the mixture (0.480 g) thus obtained was separated by preparative TLC on silica gel (ethyl acetate–hexane; 60:40). In addition to the starting material (0.092 g), there was isolated a small amount (0.020 g, 5% based on starting material consumed) of $PGF_{2\alpha}$ methyl ester 15-acetate (**5a**), and the two major products $PGF_{2\beta}$ methyl ester 15-acetate (**1b,** 0.220 g, 54%) and $PGF_{2\beta}$ methyl ester (**1c,** 0.102 g, 28%).

Compound **5a** was an oil: $[\alpha]_D$ −5.3° ($CHCl_3$); IR ($CHCl_3$) 3615, 3485, 1733, 959 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (m, 3 H), 2.00 (s, 3 H), 2.28 (t, 2 H, J = 6.5 Hz), 3.60 (s, 3 H), 3.40 (m, 1 H), 4.08 (m, 1 H), 4.53–5.49 (m, 5 H). This substance was identical in all respects with an authentic specimen prepared as described by White.[5]

Compound **1b** also was an oil: $[\alpha]_D$ −30.0° (CH_3OH); IR ($CHCl_3$) 3615, 3485, 1734, 960 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (m, 3 H), 2.03 (s, 3 H), 2.28 (t, 2 H, J = 6.4 Hz), 3.62 (s, 3 H), 3.97 (m, 2 H), 4.87–5.62 (m, 5 H). This compound was identical in all of its properties with those of a sample prepared according to White.[5]

$PGF_{2\beta}$ methyl ester **1c** was a solid which after crystallization from ethyl acetate had mp 85–86 °C (lit.[18] 90–91 °C); $[\alpha]_D$ − 4.1° (CH_3OH); IR ($CHCl_3$) 3615, 3400, 1733, 957 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (m, 3 H), 2.32 (t, 2 H, J = 6.6 Hz), 3.67 (s, 3 H), 3.94 (m, 3 H), 5.42 (m, 4 H).

Anal. Calcd for $C_{21}H_{36}O_5$: C, 68.44; H, 9.85. Found: C, 68.39; H, 9.91.

Aluminum Hydride Reduction of 11-*epi*-PGE_2 Methyl Ester 15-Acetate (3d). The reduction of **3d** was carried out in a manner identical with that described for **3c.** The crude mixture was separated by TLC on silica gel (ether–hexane, 60:40). In addition to the starting material (14%), there was isolated 11-*epi*-$PGF_{2\alpha}$ methyl ester 15-acetate (**2b,** 58% based on starting material consumed), and 11-*epi*-$PGF_{2\alpha}$ methyl ester (**2c,** 35%).

Compound **2b** was an oil: $[\alpha]_D$ + 31° ($CHCl_3$); IR ($CHCl_3$) 3625, 3535, 1732, 967 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (m, 3 H), 2.02 (s, 3 H), 2.28 (t, 2 H, J = 6.7 Hz), 3.62 (s, 3 H), 4.30 (m, 2 H), 4.94–5.73 (m, 5 H). This compound was not characterized further; instead, it was directly hydrolysed to 11-*epi*-$PGF_{2\alpha}$ as described below.

Compound **2c** was a solid which, after crystallization from ethyl acetate, had mp 110–111°; $[\alpha]_D$ +84.4° (CH_3OH); IR ($CHCl_3$) 3610, 3425, 1734, 965 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (m, 3 H), 2.30 (t, 2 H, J = 6.8 Hz), 3.67 (s, 3 H), 4.17 (m, 3 H), 5.27–5.66 (m, 4 H).

Anal. Calcd for $C_{21}H_{36}O_5$: C, 68.44; H, 9.85. Found: C, 68.34; H, 9.85.

$PGF_{2\beta}$ (1a). A. Hydrolysis of $PGF_{2\beta}$ Methyl Ester 15-Acetate (1b). To a solution of **1b** (0.220 g, 0.534 mmol) in methanol (34 ml) was added water until turbidity was achieved and then potassium carbonate (0.220 g, 1.6 mmol) was added. The solution was left at room temperature for 53 h and then it was concentrated in vacuo to one-half the original volume. Water (5 ml) was added and the neutral materials were extracted with dichloromethane (10 ml). The aqueous phase was made acidic to ca. pH 2 with saturated aqueous oxalic acid solution and the product was extracted into ethyl acetate. The extract was washed with saturated sodium chloride solution, dried over magne-

sium sulfate, and evaporated in vacuo. The residual solid (0.175 g, 93%) had mp 94–95 °C (lit.[3] 96.5–97 °C), after crystallization from ethyl acetate, and was indistinguishable from an authentic specimen[3] of $PGF_{2\beta}$.

B. Hydrolysis of $PGF_{2\beta}$ Methyl Ester (1c). The hydrolysis of **1c** was effected in the same manner as described for **1b**, with the exception that the quantity of potassium carbonate was halved. $PGF_{2\beta}$ was obtained in 94% yield and had mp 93–95 °C after crystallization from ethyl acetate.

11-*epi*-$PGF_{2\alpha}$ (2a). The hydrolysis of **2b** or **2c** was accomplished in exactly the same way as described above for **1b** and **1c**. 11-*epi*-$PGF_{2\alpha}$ (**2a**) was thus obtained in 93% yield and had mp 117–118 °C (lit.[9] 117–119 °C) after crystallization from acetonitrile. This material was indistinguishable from an authentic sample prepared according to White.[5]

Registry No.—**1a**, 4510-16-1; **1b**, 58282-71-6; **1c**, 28977-26-6; **2a**, 38432-87-0; **2b**, 61158-80-3; **2c**, 58407-22-0; **5a**, 42161-56-8; aluminum hydride, 7784-21-6.

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Synthesis of 3-Substituted Furans

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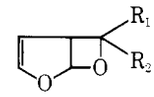
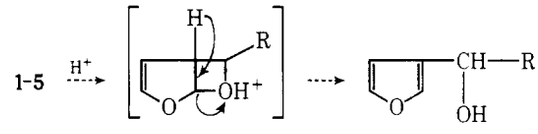
A considerable number of naturally occurring furans bear a substituent in position 3.[1] The synthetic access to them is usually not easy because of known difficulties in preparation of 3-furyl type synthons.[2] Although in recent years a number of methods for the synthesis of 3-substituted furans were reported,[3] there is still a need for further, possibly uncomplicated synthetic routes. We would like to present here a new synthesis of 3-substituted furans which is simple, does not require any special reagents or reaction conditions, and can be performed on a fairly large scale.

It is known since 1963 that carbonyl compounds can be photochemically added to furan furnishing in a remarkably regioselective reaction derivatives of 2,7-dioxabicyclo[3.2.0]-hept-3-ene.[4,5] The outcome of the photochemical cycloaddition is strongly dependent on the carbonyl compound used; the yields vary from 1% for acetophenone to 35% for benzaldehyde.[6] In this way oxetanes **1–7** were prepared (with the exception of **3**, cf. Experimental Section).



1, R_1 = H; R_2 = CH_3
2, R_1 = H; R_2 = $CO_2C_4H_9$
3, R_1 = H; R_2 = CH_2OCOCH_3
4, R_1 = H; R_2 = $CH_2CH_2CH(CH_3)_2$
5, R_1 = H; R_2 = C_6H_5
6, R_1 = R_2 = $CO_2C_2H_5$
7, R_1 = H; R_2 = 2-furyl

We have now found that oxetanes **1–5** can be isomerized in the presence of acids (e.g., *p*-toluenesulfonic acid) in aprotic solvents such as diethyl ether or carbon tetrachloride at room temperature to 3-furylmethanols **8–12** in good yields. There



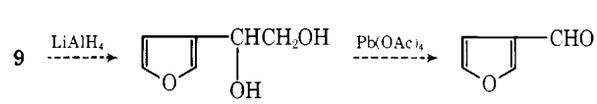
8, R = CH_3
9, R = $CO_2C_4H_9$
10, R = CH_2OCOCH_3
11, R = $CH_2CH_2CH(CH_3)_2$
12, R = C_6H_5

can be little doubt that the gain in stabilization on return to the furan system is the driving force of this isomerization. In Table I are shown the yields, boiling points, and analytical data of 3-furylmethanols obtained.

Table I. 3-Furylmethanols from Isomerization of 2,7-Dioxabicyclo[3.2.0]hept-3-enes

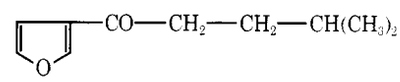
Compd	Yield, %	Bp, °C (mm)	Anal., % Calcd C	Calcd H	Found C	Found H
8	58	65–70 (0.2)	64.3	7.2	63.9	7.5
9	73	80–83 (0.15)	60.6	7.1	60.3	7.4
10	63	98–100 (0.2)	56.5	5.9	56.4	6.2
11	68	80–85 (0.2)	71.4	9.6	71.5	9.6
12	68	80–85 (0.2)	75.8	5.8	75.6	5.7

Compound **9** was reduced with lithium aluminum hydride to diol **13**, which, in turn, was cleaved with lead tetraacetate to 3-furylaldehyde **14** in 65% yield:



13 **14**

Compound **11** was oxidized with Sarett or Jones reagents to perilla ketone **15.**



15

These examples show that 3-furylmethanols can be exploited in the synthesis of naturally occurring furans either directly by employing a suitable aldehyde for photocycloaddition or by means of convenient synthons, e.g., **9**, **13**, or **14**.

The behavior of oxetanes **6** and **7** toward acids was different from that of compounds **1–5**. Whereas oxetane **6** remained unchanged under the conditions employed, oxetane **7** was very unstable; the acidity of silica gel for chromatography was sufficient to convert **7** into a new compound for which the