herein described not only provide for a unique reduction of aromatic half-esters, but can be used as a one-step method for preparing benzylic silanes containing ester groups—compounds not readily accessible at the present time.

p-**Carboethoxybenzyltrichlorosilane.**—To 10 g (52 mmol) of ethyl hydrogen terephthalate and 40 ml of acetonitrile was added 32 ml (0.32 mol) of trichlorosilane. The resulting solution was stirred at reflux for 1 hr. It was then cooled to 0° as 30 ml (0.16 mol) of tri-*n*-propylamine was rapidly added. This solution was refluxed for 16 hr, followed by addition of 500 ml of diethyl ether. After storage in a cold room for a few hours, the tri-*n*-propylamine hydrochloride precipitate was removed by filtration. Solvent removal followed by distillation *in vacuo* gave 13.4 g of product, bp 110–115° (0.85 mm), mp 72–73°, which was purified for analysis by vpc (10% SE-30 on Chromosorb A, 10 ft × $^3/_8$ in.).

Anal. Calcd for $C_{10}H_{11}Cl_3SiO_2$: C, 40.35: H, 3.73: Cl, 35.73: Si, 9.44. Found: C, 40.34: H, 3.93: Cl, 35.53: Si, 9.43.

Ethyl *p*-**Toluate.**—A solution of 9.4 g (30 mmol) of *p*-carboethoxybenzyltrichlorosilane in 100 ml of ethanol was refluxed for 1 hr. Potassium hydroxide (2.2 g, 33 mmol) in 50 ml of ethanol was added to the refluxing solution over a 15-min period. The addition was accompanied by the evolution of hydrogen chloride gas and the formation of a flocculent precipitate. An additional 4.1 g (62 mmol) of potassium hydroxide was added to make the solution just basic to Hydrion paper. After 0.5 hr at reflux, the solution was decanted and filtered. The filtrate was diluted with 500 ml of water and then extracted with four small portions of diethyl ether. The usual work-up followed by distillation resulted in 3.7 g (75%) of ethyl *p*-toluate [bp 75° (1.9 mm), lit.[5] bp 111° (13 mm)].

General Procedure for the Reduction of Half-Esters to Methyl-Substituted Carboxylic Acids.—The reduction of ethyl hydrogen terephthalate is described. The other half-esters in Table I were reduced in a similar fashion.

The procedure was the same as above up to the distillation *in vacuo*. Instead, the brown oily residue was combined with 50 ml of methanol and refluxed for 1 hr. To this mixture was added slowly with cooling 29 g (0.5 mol) of potassium hydroxide in 100 ml of methanol and 25 ml of water. The resulting mixture was refluxed for 19 hr, then diluted with 750 ml of water and filtered. The filtrate was treated with dilute hydrochloric acid until precipitation of all of the carboxylic acid was complete. The crude brown product was purified by sublimation to give 4.5 g (64% yield) of *p*-toluic acid.

Acknowledgment.—We are grateful to the National Science Foundation (GP 12049) whose financial assistance made this work possible.

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DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA 47907

ROBERT A. BENKESER*
DAVID F. EHLER

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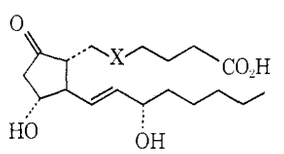
Transition Metal Ion Assisted Chromatography. Separation of Prostaglandins PGA_2 and PGB_2

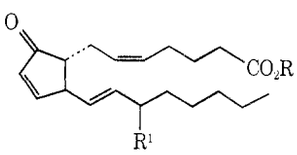
Summary: Using transition metal salts other than silver, chromatographic separations have been made that appear to be based on the metal ion complexing with carbon–oxygen double bonds.

Sir: Organic compounds differing either in number or geometry of carbon–carbon double bonds have traditionally been separated by chromatography on silver nitrate impregnated supports.[1]

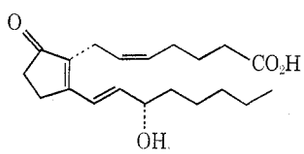
π-Complex formation between silver(I) ions and carbon–carbon double bonds forms the basis of such separations. Prostaglandins of the **2** series can be separated from those of the closely related **1** series, *e.g.*, PGE_1 (**1**) and PGE_2 (**2**), on silver nitrate systems.[2] However, this method fails[3] when applied to the difficult separation of prostaglandins PGA_2 (**3**) and PGB_2 (**4**).



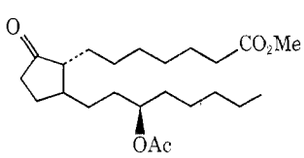
1, X = $-CH_2CH_2-$
2, X = cis-CH=CH-



3, R = H; R^1 = 15(*S*)-OH
5, R = Me; R^1 = 15(*R*)-OAc



4



6

Prostaglandin PGA_2 is easily isomerized to PGB_2 by both acid and base catalysis as well as by an isomerase in cat blood.[4] Because of this easy isomerization, methods for separating PGA_2 and PGB_2 are of importance to synthetic and metabolic studies. Such methods would also have utility for the purification of PGA_2 isolated from the coral *Plexaura homomalla*.

In the present investigation, an improved method of separation of these two compounds was sought. Precoated Brinkman tlc plates (0.25 mm, silicic acid) were impregnated with various transition metal salts by dipping the plates in a 10% solution of the salt in acetonitrile, ethanol, or a 50:50 mixture of these solvents. Table I contains the R_f values of PGA_2 (**3**),

TABLE I

R_f VALUE OF PROSTAGLANDINS ON SILICIC ACID PLATES[a] COATED WITH VARIOUS COMPLEXING METALS

Compd	Normal	$AgNO_3$	$NiCl_2$	$CoCl_2$	$FeCl_3$	$CrCl_3$
V[b]	0.36	0.41	0.37		0.34	0.37
VI[b]	0.43	0.55	0.45		0.48	0.45
PGA_2[c]	0.34	0.23	0.25	0.34	0.16	0.41
PGB_2[c]	0.34	0.27	0.25	0.35	0.23	0.41

[a] Brinkman 0.25-mm silicic acid plate. [b] 20% ethyl acetate in hexane as developing solvent. [c] 40% ethyl acetate, 1% HOAC in hexane as developing solvent.

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(2) K. Green and B. J. Samuelsson, *J. Lipid Res.*, **5**, 117 (1964).
(3) J. E. Shaw and P. W. Ramwell, *Methods Biochem. Anal.*, **17**, 325 (1969).
(4) R. L. Jones, *J. Lipid Res.*, **13**, 511 (1972).

PGB_2 (**4**), methyl 15(*R*)-acetoxy-9-oxo-5-*cis*,10,13-*trans*-prostatrienoate (**5**), and methyl 15(*R*)-acetoxyl-9-oxoprostanoate (**6**) on Brinkman silicic acid plates and on plates additionally impregnated with transition metal ions. Complexing was indicated in all systems tried except possibly for chromium(III) chloride. Iron(III)-coated plates were the only ones that were effective for the clear separation of prostaglandins PGA_2 and PGB_2. Two competing factors appear to be influencing R_f values of the compounds. A partial deactivation of the silicic acid plates caused by the coating process gives rise to increased mobility compared to normal plates [similar to that seen for silver(I) ion plates]. Competing with deactivation is complexing between the metal ions and the substrate which retards the substrate's movement on the plate.

It is interesting that **6** which contains no carbon–carbon double bonds is retarded on iron(III) plates compared to silver nitrate plates. This suggested that the separation of PGA_2 and PGB_2 on iron(III) plates might be due to factors other than simple differential complexation of the iron(III) with the carbon–carbon double bonds of PGA_2 and PGB_2.[5]

It was demonstrated that 3,7,12-triketochlolanic acid is strongly retarded on iron(III) tlc plates (R_f 0.22, EtOAc–Bz–HOAc, 49.75:49.75:0.50) relative to uncoated plates (R_f 0.65) and plates coated with silver nitrate.[6] Ergosterol, however, was strongly retarded on silver nitrate plates (R_f 0.20, 17% EtOAc–hexane) relative to uncoated plates (R_f 0.38). Ergosterol (R_f 0.67) was only slightly retarded on iron(III) plates compared to cholesterol using 17% EtOAc–hexane as developing solvent. The $FeCl_3$ plates appear somewhat deactivated toward both sterols relative to uncoated plates.

Several different columns were tested for extending the results obtained from tlc to preparative column chromatography. On a column packed with a support made from 10% $FeCl_3$ coated on silicAR CC-4, elimination of the C-15 acetoxy group was complete during the time necessary for chromatography of the diester of 15-epi-PGA_2 (**5**) (obtained from *Plexaura homomalla*)—obviously iron(III) effects this elimination. Attempted purification of 15 epi-PGA_2 by chromatography over an iron(III)-impregnated column required large amounts of ethyl acetate in the eluting solvent mixture (75:25, hexane–ethyl acetate). This led to the elution of $FeCl_3$ as well as the prostaglandin. Probably this drawback can be overcome by using other solvents or a less soluble iron(III) salt. It was found that 10% $CuCl_2$ on silicic acid was effective for the purification of the sample of prostaglandin 15-epi-PGA_2 from *Plexaura homomalla*. This sample contained several small peaks by glc (as methyl esters) which were not separated by further column chromatography on silicic acid supports.[7] Chromatography on 10% $CuCl_2$ supported on silicAR CC-4 (support to sample ratio of 50:1) using a solvent of 25% ethyl acetate in hexane was sufficient to elute 15-epi-PGA_2 [217 nm (ϵ 10,800)] essentially pure by glc. Indications were any minor impurities could be removed using a higher support to compound ratio.

(5) R. L. Spraggins, *Proc. Food Drugs Sea Conf.*, **3**, in print (1972).

(6) Work done in the laboratory of Professor A. K. Bose (Stevens Institute of Technology) by Robert L. Spraggins and John J. Savarese.

(7) R. L. Spraggins, Doctoral Dissertation, University of Oklahoma, 1970.

(8) Now Research Scientist at Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Castle Point Station, Hoboken, N. J. 07030.

ALZA RESEARCH
PALO ALTO, CALIFORNIA 94304

ROBERT L. SPRAGGINS*[8]

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