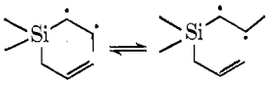
Alternative mechanisms for the interconversion of **3** and **5** have been considered. It is well known that cis–trans isomerization of olefins[18] occurs upon heating to sufficiently high temperature, presumably *via* a biradical intermediate. To evaluate this possibility, a model compound, *cis,trans*-propenyltrimethylsilane[13] was prepared and thermolyzed. It was found that nearly 100° higher temperatures were required to effect isomerization. This result could have been anticipated if the activation parameters were similar to those of the diradical course of 2-butene thermal isomerization (E_a = 63 kcal/mol, log A = 13.8).[25] It would suggest that a reaction course for isomerization of **3** to **5** passing through the diradical intermediate **8** would have an



8

activation requirement >20 kcal higher than observed. Several other alternative mechanistic possibilities can be regarded as unlikely, and in the interests of brevity will not be discussed.

This work clearly indicates that the enhanced ability of silicon to participate in pericyclic transition states may lead to the reversible or irreversible formation of multiply bonded silicon.

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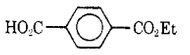
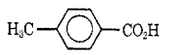
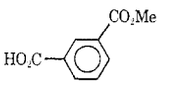
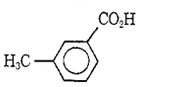
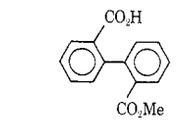
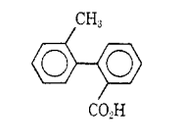
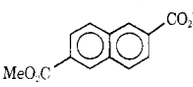
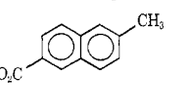
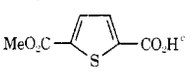
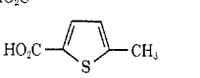
Selective Reduction of Aromatic Carboxyl Groups to Methyl in the Presence of Ester Functionality. A New Procedure for the Preparation of Ester-Containing Organosilanes

Summary: New synthetic procedures for the selective reduction of the carboxyl group of aromatic half-esters to methyl and for the preparation of benzylic silanes containing ester groups is described.

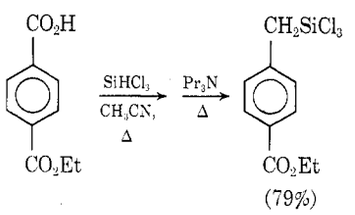
Sir: It is well documented that ester groups can usually be reduced with relative ease while carboxyl groups are relatively resistant to reduction. Further, reduction of a carboxyl group usually results in the production of aldehydes[1] or alcohols.[2]

Previously[3] we reported the unprecedented reduction of aromatic carboxyl groups directly to methyl groups by the use of a trichlorosilane–*tert*-amine combination. In an endeavor to extend the scope of this reduction, we attempted to reduce aromatic esters under the same conditions. Surprisingly, esters like ethyl benzoate and phenyl benzoate were totally unreactive and could be recovered virtually unchanged.[4] This immediately raised the possibility that aromatic half-esters might be made to undergo reduction of the carboxyl group to a methyl while the ester group would be left intact. Accordingly the "one-pot" reduction procedure developed earlier[3] was applied to a representative series of aromatic half-esters with the results depicted in Table I. As will be noted from this table the unreduced ester groups were saponified by the base treatment employed to cleave the intermediate benzylic silanes. In the case of ethyl hydrogen terephthalate (entry 1 of table) the intermediate benzylic silane was isolated and characterized in a 79% yield. Benzylic silicon–carbon cleavage of this product was achieved

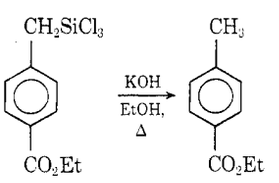
TABLE I
SELECTIVE REDUCTION OF AROMATIC HALF-ESTERS

Entry	Half-ester	Product[a]	Yield[b], %
1			64
2			42
3			41
4			37
5			26

[a] Satisfactory agreement with literature melting points and spectral correlations were obtained for all products. [b] Based on weight of starting half-ester. [c] New compound which gave satisfactory analysis and spectral correlation.



with a slight excess of base in only 0.5 hr. to give a 75% yield of *p*-ethyl toluate. The ester was not saponified under these conditions.



While this investigation is still in its preliminary stages, the results to date suggest that the procedures

(1) S. Ono and T. Yamauchi, *Bull. Chem. Soc. Jap.*, **25**, 404 (1952); H. A. Staab and H. Braunling, *Justus Liebigs Ann. Chem.*, **654**, 119 (1962).

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(4) Unpublished studies by Robert T. Roche of our laboratory.

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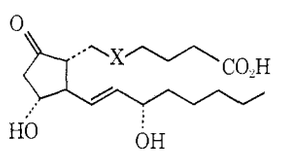
Transition Metal Ion Assisted Chromatography. Separation of Prostaglandins PGA_2 and PGB_2

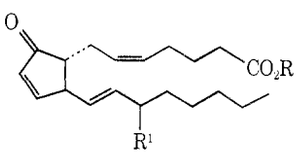
Summary: Using transition metal salts other than silver, chromatographic separations have been made that appear to be based on the metal ion complexing with carbon–oxygen double bonds.

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]

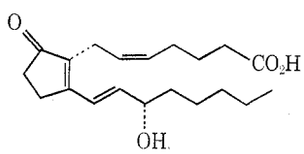
π-Complex formation between silver(I) ions and carbon–carbon double bonds forms the basis of such separations. Prostaglandins of the **2** series can be separated from those of the closely related **1** series, *e.g.*, PGE_1 (**1**) and PGE_2 (**2**), on silver nitrate systems.[2] However, this method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



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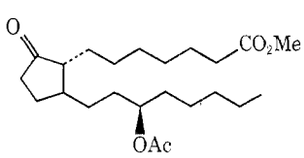

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Prostaglandin PGA_2 is easily isomerized to PGB_2 by both acid and base catalysis as well as by an isomerase in cat blood.[4] Because of this easy isomerization, methods for separating PGA_2 and PGB_2 are of importance to synthetic and metabolic studies. 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.

(1) C. B. Barrett, M. S. J. Dallas, and F. B. Padley, *Chem. Ind. (London)*, 1050 (1962).
(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).