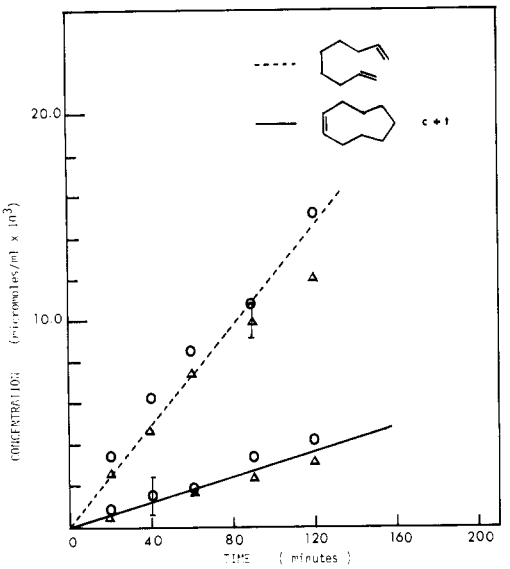


Figure 1. Composite plot of product concentration vs. time in the photolysis of bicyclo[6.1.0]nonanes: ○, *trans*-bicyclo[6.1.0]-nonane; △, *cis*-bicyclo[6.1.0]nonane; reactions in pentane solution; 185-nm radiation.

vertical bars on two of the points. Within the experimental uncertainty, the rates are seen to be the same whether the starting material is **2** or **3**. But the ratio of *trans*- to *cis*-cyclononene was not the same in both instances, the values being 0.45 and 0.80 from the cis and trans isomers. Since all of the useful radiation (185 nm) was totally absorbed by the reactant (at least at zero time) in these experiments, the rates may be considered to be proportional to the quantum yields. The apparent curvature for the yield of 1,8-nonadiene in the photolysis of the cis isomer is not only within the experimental uncertainty but is also at conversions at which the product must be absorbing the incident light to undergo secondary decomposition.

The photolysis of **2** in pentane solution at 214 nm was also studied. In this instance also, the products were the same (eq 2) as those in photolysis at 185 nm. The ratio of 1,8-nonadiene to cyclononene (cis plus trans) was 5.0 compared to the value of 4.3 at 185 nm. There was no indication of the isomerization of **2** to **3**.

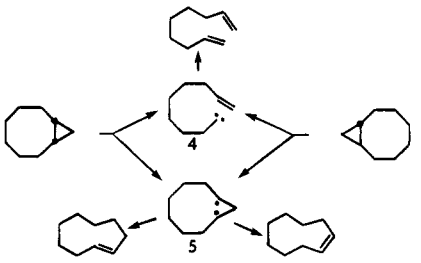
The photolysis of cyclononene in pentane solution at 185 nm was also investigated. Initially there was a rapid stereoisomerization reaction from either the cis or trans isomer to the other stereoisomer. The photostationary ratio may be considered to be quite close to a value of 0.90 although the formation of side products became noticeable well before this ratio was reached.

Discussion

The striking points in the present work are (i) the total similarity in the photochemistry of **2** to that of **3** in all but one detail and (ii) the absence of a stereoisomerization induced by light from **2** to **3** (or vice versa) in contrast to the ease with which this reaction occurs in cyclooctene.[3] These points will be discussed in order.

The similarity between **2** and **3** in their photochemical behavior is both qualitative and quantitative. It is best explained in terms of common intermediates as in Scheme I. This picture is consistent with earlier results[1,7] on the photochemistry of cyclopropanes in solution. But the single inexplicable feature that was found earlier, viz., the different ratios of trans to cis olefins that were obtained

Scheme I



from the cis and trans reactants, persists in the present system. It may be observed that these ratios are not identical with the value at the photostationary state of cyclononene itself.

It is possible that the two-bond break *follows* the one-bond break as proposed by Rossi[8] from a theoretical analysis of the excited state of cyclopropane. In this instance, Scheme I should be rearranged to show **5** as the precursor to **4**. The fact that 1,8-nonadiene is the major product further indicates that there is a strong tendency for **5** to go to **4** and then to 1,8-nonadiene, much less of a tendency to rearrange to cyclononene, and virtually no tendency to reclose to the starting material. This would rationalize the failure to detect any stereoisomerization of **2** to **3** or **3** to **2**. It is tempting to view the two-bond cleavage as a reaction which would require more (activation) energy than the one-bond cleavage but the use of 214-nm radiation shows that in this instance there is more, not less, 1,8-nonadiene relative to cyclononene! Many of these uncertainties may be related to an emerging view[9] that the decomposition pathways in organic photochemistry in the far-ultraviolet are quite sensitive to small changes (1–2 kcal/mol) in the energy of the photon and hence to the level of excitation of the reacting molecule. These ideas are currently under investigation.

It is relevant to mention here that the photolysis of cyclononene with 185-nm radiation *in the vapor phase* has been studied before.[10] The products that were observed were 1,8-nonadiene and vinylcycloheptane in the ratio of 2:1. Since, in this work, *cis*- and *trans*-cyclononene were not separated from each other, it was not possible to observe any stereoisomerization. The present results show that the vapor-phase reaction bears little relationship to the reaction in solution.

Registry No. **2**, 13757-43-2; **3**, 39124-79-3.

(7) R. Srinivasan and J. A. Ors, *J. Am. Chem. Soc.*, **100**, 7089 (1978).
(8) A. R. Rossi, *J. Phys. Chem.*, **83**, 2554 (1979).
(9) R. Srinivasan and A. R. Rossi, to be submitted for publication.
(10) Y. Inoue, S. Takamuku, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **49**, 1147 (1976).

Aromatic Substitution: Regiospecific Synthesis of Highly Substituted Diphenyl Sulfones

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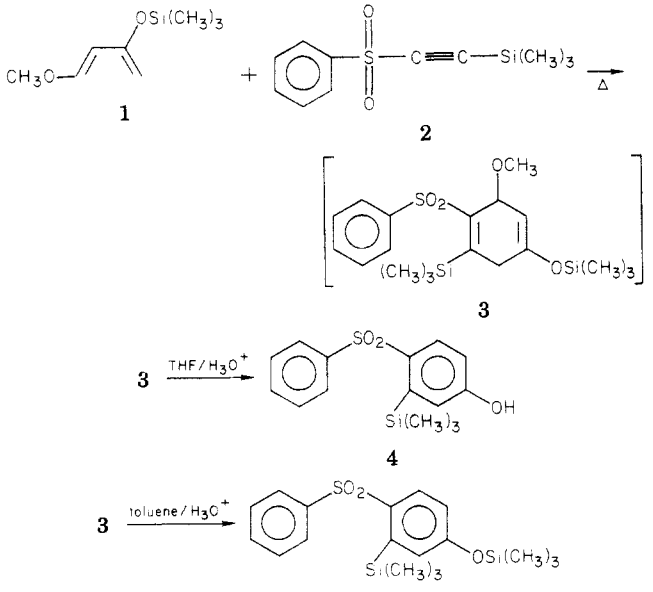
The preparation of specifically substituted aromatic rings ranks as one of the oldest and most continually studied problems of organic synthesis. Although many general, efficient, highly workable methods have been developed, there remain specific areas where these classical

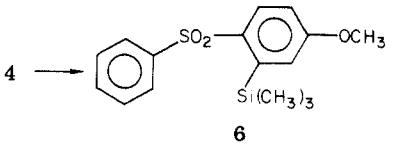
0022-3263/81/1946-1951$01.25/0

methods remain more or less inadequate. A particular problem is that of regiospecificity. Preparation of highly substituted benzenoid systems, free of positional isomers, in a rational and controlled fashion is still a considerable challenge in many instances. During the course of our research we had occasion to prepare a group of highly substituted diphenyl sulfones and thereby study methods for their regiospecific preparation. This note describes our results.

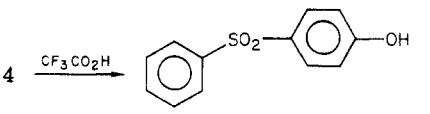
The synthetic plan was to capitalize on the regiospecificity of the Diels–Alder reaction to prepare an initial aromatic substrate, which could then be further substituted by other techniques. Judicious choice of diene and dienophile should lead to aromatic functionality capable of directing further substitution. To this end, Danishefsky's diene (1)[1] and an acetylenic sulfone 2[2] were refluxed in toluene until reaction was complete. The initial product, presumably diene 3, was not isolated but directly hydrolyzed to aromatic products. Single-phase hydrolysis (THF, 10% HCl, room temperature) afforded sulfonylphenol 4, while two-phase hydrolysis (toluene/5% HCl, 0 °C) gave the corresponding trimethylsiloxy compound 5. No isomers were formed.



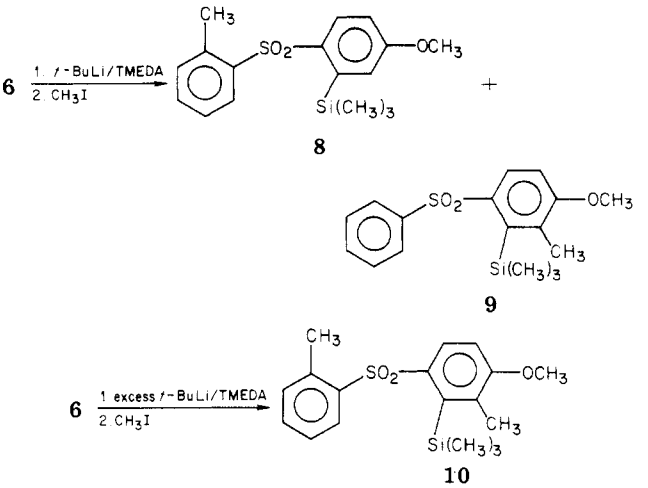
The structural assignments for these compounds rest on their NMR spectra[3] and on an analogy to Danishefsky's results with acetylenic dienophiles. To facilitate further manipulation, phenol 4 was protected as its methyl ether 6.



The aromatic trimethylsilyl group had been introduced as a protecting and/or activating group (vide infra), and it was of interest to test potential methods for its removal. As expected, sulfonylanisole 6 proved quite inert to nucleophiles such as methyllithium and tetrabutylammonium fluoride. Conversely, (trimethylsilyl)phenol 4 was smoothly deprotected with trifluoroacetic acid to afford phenol 7.[4]



It has been shown that the protons ortho to both aromatic sulfones[5] and anisoles[6] are acidic enough to allow metalation at these ortho positions. Such a metalation was attempted with (trimethylsilyl)anisole 6. Treatment with *t*-BuLi/TMEDA (THF, −78 °C) followed by prompt quenching with methyl iodide afforded mixtures of two products. At short reaction times (1–15 min) the major product was methyl sulfone 8. As reaction times increased, production of the coproduct, methylanisole 9, increased. If the metalation was allowed to equilibrate for 3 h prior to quenching, 9 was the sole product. At no time was 8 the exclusive product. Treatment of 6 with a large (10-fold) excess of *t*-BuLi/TMEDA, followed by quenching with methyl iodide, produced the dialkylated material 10.

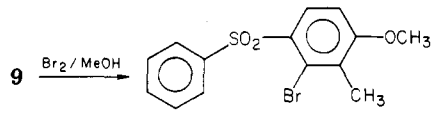


The structural assignments for these compounds rest on their ^{1}H NMR spectra. At 270 MHz the aromatic portions of these spectra are nearly first order and readily interpretable.[7]

These alkylation results seem to suggest an initial partitioning between two lithiated species (pre-8 and pre-9) which eventually equilibrate to the single intermediate from which 9 arises. That the sterically hindered 9 is the thermodynamic product indicates that the trimethylsilyl group imparts a good measure of electronic stabilization to the intermediate lithio compound. This directing effect is of synthetic import for it allows regiospecific substitution at the most sterically hindered of three potentially acidic sites. In addition, the trimethylsilyl group serves as a "handle" for the electrophilic elaboration of further functionality.[4] For example, treatment of 9 with bromine in methanol cleanly gave rise to bromo sulfone 11, itself capable of further transformations.

Although the generality of the methodology described here has yet to be rigorously demonstrated, there is con-

(1) S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.* **96**, 7807 (1974).
(2) S. N. Bhattacharya, B. M. Josiah, and D. R. M. Walton, *Organomet. Chem. Synth.*, 1, 145 (1970/1971).
(3) Particularly revealing for these compounds was a one-proton signal around δ 7.0, which appeared as a doublet of doublets, J = 8 and J = 2 Hz, assigned as the proton at C-6 (phenol numbering).
(4) C. Earborn, *J. Organomet. Chem.*, **100**, 43–57 (1975), and references cited therein.
(5) (a) H. Watanabe, R. L. Gay, C. R. Hauser, *J. Org. Chem.*, **33**, 900 (1968). (b) D. Hellwinkel and M. Supp, *Chem. Ber.*, **109**, 3749 (1976). (c) A. R. Acharekar, V. N. Gogte, and B. D. Tilak, *Ind. J. Chem., Sect. B.*, **15**, 408 (1977).
(6) H. Gilman and J. W. Morton, Jr., *Org. React.*, **8**, 258 (1954), and references cited therein.
(7) The 270-MHz ^{1}H spectra of compounds 8–10 were recorded at the University of Chicago. We are indebted to Professor W. H. Urry for these measurements as well as for his collaboration as to their interpretation.



11

siderable synthetic potential. A 1,2,3,4-tetrasubstituted benzene has been prepared in a regiospecific, rational fashion. Extension of these procedures (e.g., both dienes and dienophiles with extended functionality, use of other alkylating or acylation agents, other electrophiles, etc.) for the preparation of highly substituted aromatics is under study. In addition, it is expected that reduction of these aromatic species will ultimately lead to highly functionalized cyclohexenones of considerable synthetic utility.

Experimental Section

General Procedures. Melting points were determined on a Laboratory Devices mel-temp apparatus and are uncorrected. Nuclear magnetic resonance spectra (NMR) were recorded on Varian T-60 and EM-360 and JEOLCO FX 100 spectrometers, using tetramethylsilane as an internal standard. Combustion analyses were performed by Atlantic Microlabs. Column chromatography was accomplished on ICN Woelm silica gel, 70–230 mesh. High-pressure liquid chromatography (LC) was performed with EM Lobar prepacked LiChroprep silica gel columns. Evaporative bulb-to-bulb distillations were performed with a Buchi Kugelrohr hot-air oven. The boiling points reported for this technique are therefore the oven temperature at which distillation occurred. The drying process referred to in the workup procedure involved swirling the solution over an excess amount of anhydrous magnesium sulfate, followed by filtration. Anhydrous solvents were distilled from appropriate reagents under argon and stored in Schlenk flasks. The yields reported are of analytically pure material. No attempt has been made to maximize them.

4-(Benzenesulfonyl)-3-(trimethylsilyl)phenol (4). A solution of 5 g (21 mmol) of sulfonylacetylene **2** and 3.6 g (21 mmol) of Danishefsky's diene (**1**) in 150 mL of anhydrous toluene was refluxed under argon. The reaction was monitored by gas chromatography and sufficient diene was further added to ensure complete consumption of the acetylene. At completion the solution was cooled, concentrated, and partitioned between equal volumes of THF and 10% hydrochloric acid. After being stirred for 4 h the mixture was diluted with ethyl acetate. The layers were separated, and the organic phase was washed with water and dried. Concentration afforded a crude crystalline product which was triturated with toluene to give 3 g (45%) of phenol **4** as a white, crystalline solid: mp 156–158 °C; NMR ($CDCl_3$) δ 0.36 (s, 9 H), 6.40 (br s, 1 H), 7.00 (d of d,[3] J = 9, J = 2 Hz, 1 H), 7.30–7.90 (m, 9 H).

Anal. Calcd for $C_{15}H_{18}O_3SSi$: C, 58.79; H, 5.92; S, 10.46. Found: C, 58.73; H, 5.94; S, 10.44.

1-(Benzenesulfonyl)-2-(trimethylsilyl)-4-(trimethylsiloxy)benzene (5). A solution of 1 g (4.2 mmol) of sulfonylacetylene **2** and 1.08 g (6.3 mmol) of Danishefsky's diene (**1**) in 15 mL of anhydrous toluene was refluxed and monitored as described above. When reaction was complete the solution was cooled to 0 °C and 10 mL of 5% hydrochloric acid was added. After the mixture was stirred for 20 min, the layers were separated, and the organic phase was washed with 5% sodium hydroxide solution. The organic fraction was dried, concentrated, and subjected to evaporative bulb-to-bulb distillation, affording 1 g (63%) of diphenyl sulfone **5** as a pale yellow oil: bp 180 °C (0.15 mm); NMR ($CDCl_3$) δ 0.18 (s, 9 H), 0.41 (s, 9 H), 6.97 (d of d, J = 8, J = 3 Hz, 1 H), 7.20 (d, J = 3 Hz, 1 H), 7.42–8.00 (m, 6 H).

Anal. Calcd for $C_{18}H_{26}O_3SSi_2$: C, 57.10; H, 6.92; S, 8.47. Found: C, 57.09; H, 6.94; S, 8.41.

4-(Benzenesulfonyl)-3-(trimethylsilyl)anisole (6). A solution of 1.85 g (6.03 mmol) of phenol **4**, 1.7 g (12 mmol) of methyl iodide, and 1.65 g (12 mmol) of potassium carbonate in 50 mL of acetonitrile was heated at 50 °C for 4 h. The solution was cooled, diluted with ethyl acetate, washed twice with water, dried, and concentrated to an oil. Evaporative bulb-to-bulb distillation gave 1.6 g (79%) of anisole **6** as an oil: bp 180 °C (0.1 mm); NMR ($CDCl_3$) δ 0.37 (s, 9 H), 3.78 (s, 3 H), 7.05 (d of d, J = 8, J = 2 Hz, 1 H), 7.26–7.95 (m, 7 H).

Anal. Calcd for $C_{16}H_{20}O_3SSi$: C, 59.96; H, 6.29; S, 10.00. Found: C, 60.06; H, 6.30; S, 9.94.

4-(Phenylsulfonyl)phenol (7). A solution of 1.5 g of sulfonylphenol **4** in 15 mL of trifluoroacetic acid was stirred under nitrogen for 6 h at ambient temperature. The solvent was removed in vacuo to afford a crude solid. Recrystallization from toluene provided 0.7 g (61%) of phenol **7**: mp 158–160 °C; NMR ($CDCl_3$) δ 6.90–8.10 (m, 10 H).

Anal. Calcd for $C_{12}H_{10}O_3S$: C, 61.52; H, 4.30; S, 13.69. Found: C, 61.35; H, 4.35; S, 13.61.

4-[(2-Methylphenyl)sulfonyl]-3-(trimethylsilyl)anisole (8) and 4-(Phenylsulfonyl)-3-(trimethylsilyl)-2-methylanisole (9). In an oven-dried 500-mL three-neck flask under argon was dissolved 4 g (12.5 mmol) of sulfonylanisole **6** and 3.62 g (31.2 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in 200 mL of anhydrous THF. The resulting solution was cooled, with stirring, in a dry ice/acetone bath and 16.2 mL of 1.9 M *t*-BuLi solution in pentane (Alfa-Ventron, used without independent standardization) was added via syringe over a 3-min period. Stirring was continued for an additional 12 min, whereupon the reaction was quenched with 8.52 g (60 mmol) of methyl iodide. (In other, similar runs this quench was carried out as soon as 60 s after the end of the addition of the *t*-BuLi solution. There was no change in the product ratios obtained.) The cooling bath was removed and stirring continued for an additional 2 h as the solution reached room temperature. The mixture was diluted with ethyl acetate, washed twice with water, dried, and concentrated to afford the crude product. This was subjected to high-pressure LC with 5% ethyl acetate/cyclohexane as the eluant. The first fraction obtained was 150 mg of dialkylated anisole **10** (vide infra). The second fraction was 1.3 g (31%) of anisole **9**, crystallized from cyclohexane: mp 103–105 °C; NMR ($CDCl_3$) δ 0.44 (s, 9 H), 2.13 (s, 3 H), 3.81 (s, 3 H), 7.06 (d, J = 8.4 Hz, 1 H), 7.45 (tt, J = 7.1 Hz, 2 H), 7.53 (tt, J = 7.1 Hz, 1 H), 7.71 (dt, J = 7.0, J = 2.1 Hz, 2 H), 7.73 (d, J = 8.4 Hz, 1 H).

Anal. Calcd for $C_{17}H_{22}O_3SSi$: C, 61.04; H, 6.63; S, 9.59. Found: C, 60.92; H, 6.69; S, 9.56.

In similar runs, if the reaction was stirred for 3 h at −78 °C before quenching with methyl iodide; anisole **9** was the exclusive product (74%).

The third product obtained was 1.94 g (46%) of anisole **8** as an undistilled oil: NMR ($CDCl_3$) δ 0.41 (s, 9 H), 2.42 (s, 3 H), 3.70 (s, 3 H), 6.96 (d, J = 2.5 Hz, 1 H), 7.04 (dd, J = 8.4, J = 2.5 Hz, 1 H), 7.27 (d, J = 6.9 Hz, 1 H), 7.30 (t, J = 8.0 Hz, 1 H), 7.47 (td, J = 7.5, J = 1.0 Hz, 1 H), 7.74 (d, J = 8.3 Hz, 1 H), 7.76 (d, J = 7.6 Hz, 1 H).

Anal. Calcd for $C_{17}H_{22}O_3SSi$: C, 61.04; H, 6.63; S, 9.59. Found: C, 61.04; H, 6.68; S, 9.63.

4-[(2-Methylphenyl)sulfonyl]-3-(trimethylsilyl)-2-methylanisole (10). A solution of 1 g (3.12 mmol) of anisole **6** and 3.62 g (31.2 mmol) of TMEDA in 50 mL of anhydrous THF was cooled with stirring to −78 °C. To this solution was added 16.2 mL of 1.9 M *t*-BuLi solution in pentane dropwise via syringe. The resulting mixture was stirred for 2 h and then quenched with 5 mL of methyl iodide. The cooling bath was removed, and stirring continued an additional 2 h. The suspension was diluted with ether, washed twice with water, dried, and concentrated to an oil. Chromatography on silica gel (10% ethyl acetate/cyclohexane) afforded 1.05 g (96%) of dialkylated anisole **10**: NMR ($CDCl_3$) δ 0.42 (s, 9 H), 2.01 (s, 3 H), 2.16 (s, 3 H), 3.81 (s, 3 H), 7.08 (d, J = 8.4 Hz, 1 H), 7.18 (d, J = 7.5 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 1 H), 7.41 (t, J = 7.5 Hz, 1 H), 7.71 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 7.5 Hz, 1 H).

Anal. Calcd for $C_{18}H_{24}O_3SSi$: C, 62.03; H, 6.94; S, 9.20. Found: C, 61.85; H, 6.97; S, 9.14.

4-(Phenylsulfonyl)-3-bromo-2-methylanisole (11). To a solution of 0.85 g (2.55 mmol) of alkylated anisole **9** in 10 mL of methanol was added 0.42 g (2.55 mmol) of bromine. After 3 h of stirring the reaction was roughly 50% complete. Another 0.42 g of bromine was added and stirring continued 18 h. The solution was concentrated to afford a solid. Trituration with methanol gave 0.67 g (78%) of bromoanisole **11** as a white crystalline solid: mp 121–124 °C; NMR ($CDCl_3$) δ 2.66 (s, 3 H), 3.83 (s, 3 H), 6.05

(d, J = 9 Hz, 1 H), 7.40–7.60 (m, 4 H), 7.75–8.00 (m, 2 H).

Anal. Calcd for $C_{14}H_{13}BrO_3S$: C, 49.28; H, 3.84; S, 9.40. Found: C, 49.24; H, 3.87; S, 9.40.

Acknowledgment. I thank Dr. Ray Grabiak, Professor Peter Beak, and Professor W. Urry for their helpful discussions.

Registry No. 1, 59414-23-2; 2, 32501-93-2; 4, 76741-80-5; 5, 76756-18-8; 6, 76741-81-6; 7, 7402-69-9; 8, 76756-19-9; 9, 76741-82-7; 10, 76741-83-8; 11, 76741-84-9.

Practical Synthesis of 6a-Carbaprostaglandin I_2[1]

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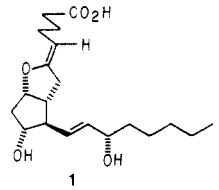
Received November 10, 1980

Prostacyclin (PGI_2, 1),[2] a recently discovered metabolite of arachidonic acid, appears to have an important role in preventing stroke, thrombosis, and heart attack.[3] However, because of the labile enol ether linkage, prostacyclin is a very unstable compound, and a chemically stable analogue would be potentially a much more useful therapeutic agent. Currently the intense search for such a stable mimic has focused upon 6a-carbaprostaglandin I_2 (**2**)[4] which has recently been shown to have a very similar biological profile to PGI_2.[5]



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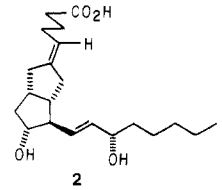

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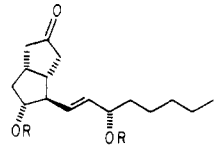
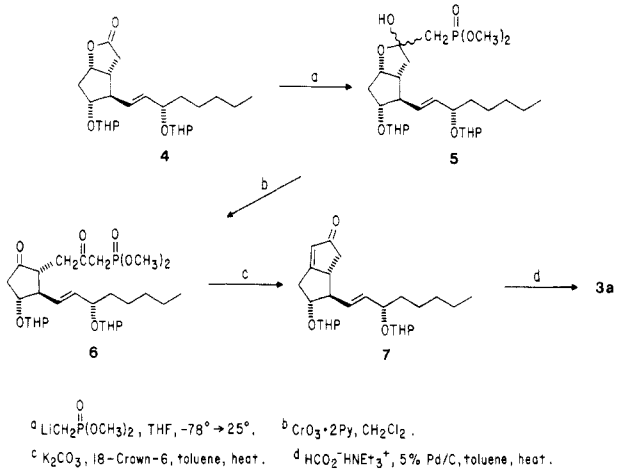


3a R = THP
3b R = H

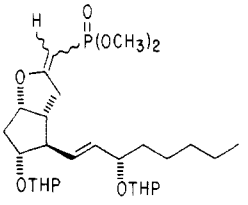
The synthesis of 6a-carba-PGI_2 was first reported in 1978 independently by Morton, Gandolfi, Nicolaou, and Kojima.[6] Since then several additional syntheses have appeared.[7] However, most of these syntheses require many steps and produce racemic material. An efficient synthesis suitable for the large-scale preparation of this important compound is still needed. A key intermediate in all except one of the aforementioned syntheses is the bicyclo[3.3.0]octanone compound **3**. This compound is then transformed to 6a-carba-PGI_2 by a Wittig reaction with (4-carboxybutyl)triphenylphosphorane. Herein is reported an efficient synthesis of optically active **3** utilizing a novel Wadsworth–Emmons reaction (see Scheme I).

Scheme I

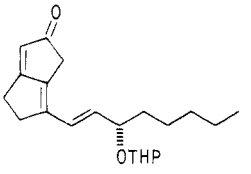


[a] $LiCH_2P(OCH_3)_2$, THF, −78° → 25°. [b] $CrO_3 \cdot 2Py$, CH_2Cl_2. [c] K_2CO_3, 18-Crown-6, toluene, heat. [d] $HCO_2^-HNEt_3^+$, 5% Pd/C, toluene, heat.

The readily available and optically pure lactone bis(tetrahydropyranyl ether) **4**, a general synthetic intermediate for the natural prostaglandins,[8] was utilized as starting material for the synthesis of 6a-carbaprostaglandin I_2. Treatment of lactone **4** with lithium dimethyl methylphosphonate[9] in tetrahydrofuran at −78 °C furnished the crystalline hemiketal **5** in 79% yield (99% yield based on recovered starting lactone). A modified Collins oxidation[10] of **5** afforded the desired diketone **6** in 64% yield along with 32% of the enol ether byproduct **8** formed from the β elimination of water from **5**. Carefully controlled Jones oxidation of **5** at −15 to −10 °C yielded 50% of **6** (63% based on recovered hemiacetal) and only 3% of byproduct **8**. Most other oxidation methods gave enol ether **8** as the major product.



8



9

Cyclization of ketone **6** to the strained bicyclo[3.3.0]octenone **7** could not be accomplished by using standard methods.[11,25] A variety of procedures were investigated for this intramolecular Wadsworth–Emmons reaction including sodium hydride in glyme or toluene, potassium carbonate in *tert*-butyl alcohol, and *n*-butyllithium in

(1) This work was described in part at the 180th National Meeting of the American Chemical Society, Las Vegas, NV, Aug 1980; Abstract No. ORGN 236.

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