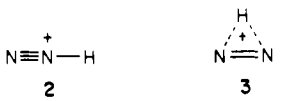
by Pople and co-workers[8] has shown that linear structure **2** is more stable than the bridged one **3**. In the course of nitrogen fixation[9,10]



2 **3**

it is highly unlikely that proton transfer to free nitrogen occurs. Instead, such proton transfer probably occurs on to coordinated dinitrogen on a suitable transition-metal site such as molybdenum. In continuation of our studies on substituted diazonium ions (such as $N_2^+NH_2$,[11] $N_2^+NO_2$,[12] N_2^+CN,[12] N_2^+F[12], etc.) we would like to report new results on our attempts to generate diazonium ion **1** not by direct protonation but by diazotization of ammonia and some of its derivatives using nitrosonium tetrafluoroborate salt.

It is known that aromatic as well as aliphatic amines and isocyanates react with NO^+ salts, such as $NO^+BF_4^-$ to form the corresponding diazonium ions.[13] Weiss recently reported[14] a useful

$$RNH_2 + NO^+BF_4^- \rightarrow RN^+ \equiv NBF_4^- + H_2O$$

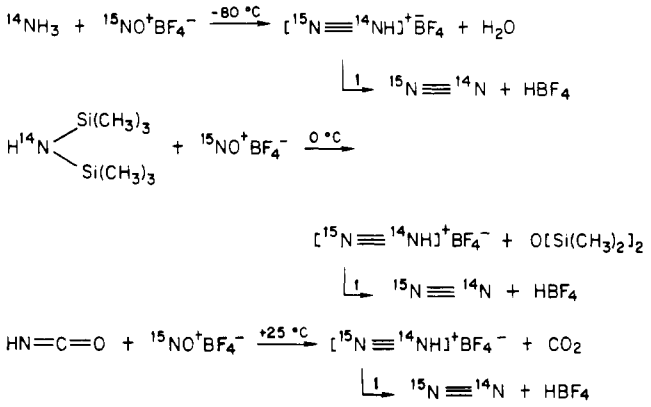
$$RN{=}C{=}O + NO^+BF_4^- \rightarrow RN^+ \equiv NBF_4^- + CO_2$$

additional anhydrous diazotization method by reacting bissilylated amines with NO^+ salt.

$$R{-}N(Si(CH_3)_3)_2 + NO^+X^- \rightarrow RN^+ \equiv N\ X^- + [(CH_3)_3Si]_2O$$

As the direct protonation of nitrogen could not be achieved in solution, it occurred to us that the problem could be attacked by generating protonated dinitrogen, i.e., the parent diazonium ion via diazotizing ammonia and some of its derivatives.

Using 96% enriched $^{15}NO^+BF_4^-$ salt[15] we have indeed succeeded with diazotization of ammonia, bis(trimethylsilyl)amine, and isocyanic acid, respectively, resulting in the formation of $^{14}N{\equiv}^{15}N$. The mono ^{15}N-labeled nitrogen gas obtained can be produced only through the intermediacy of the parent diazonium ion **1**.



All reactions were carried out in dichloromethane solution and the nitrogen evolved during the reaction was analyzed by GC-MS.[16] Ammonia itself reacts with nitrosonium tetrafluoroborate rather violently even at −80 °C to give 89% monolabeled and 11% unlabeled dinitrogen. In reaction of bis(trimethylsilyl)amine 94% monolabeled nitrogen was formed, the reaction being somewhat sluggish at −80 °C. Isocyanic acid reacted very slowly with the nitrosonium ion even at room temperature. A competing polymerization of isocyanic acid seem to occur along with the diazotization and it was not possible to determine the exact isotope distribution of the evolved nitrogen although it is estimated to be ≥90% monolabeled.

Attempts were made to directly detect the monolabeled diazonium ion **1** using ^{15}N NMR spectroscopy.[17] In a typical experiments ≈50 mg of bis(trimethylsilyl)amine was treated with ≈100 mg of 95% $^{15}NOBF_4^-$ in 2 mL of dichloromethane in a 10-mm NMR tube at −80 °C in the NMR probe. The probe temperature when raised to −40 °C resulted in slow evolution of nitrogen gas. Accumulation of ^{15}N data over a period of 30 min detected, however, the presence of only $^{15}NO^+$ salt and no signal for **1** could be observed. The failure to detect HN_2^+ in the described stop-flow experiment seems to indicate that **1** is unstable under the reaction conditions. This is in accordance with the known low proton affinity of dinitrogen.

Our studies reported indicate that the parent diazonium ion **1** was in situ formed in the diazotization of ammonia and its derivatives with $^{15}NO^+BF_4^-$. However, **1** once formed has very short lifetime to be observed by NMR spectroscopy and spontaneously deprotonates to $^{15}N{\equiv}^{14}N$.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged. R. Herges is grateful for the financial support by a Feodor Lynen grant of the Alexander von Humbold Foundation.

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(15) 96% ^{15}N enriched $NO^+BF_4^-$ was prepared by treating 96% $^{15}NOCl$ with $HF{-}BF_3$ in nitromethane solution at −78 °C. The 96% $^{16}NOCl$ was generated by treating 96% $Na^{15}NO_2$ with dry HCl in nitromethane solvent with $CaCl_2$ drying.

(16) GC-MS analysis was performed on a Hewlett-Packard 5985 A GC-MS spectrometer.

(17) The ^{15}N NMR studies were carried out on a Varian Associates Model FT-80 NMR spectrometer equipped with a variable-temperature broad-band probe.

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Total Synthesis of the Cytochrome P-450 Epoxygenase Metabolites 5(*R*),6(*S*)-, 5(*S*),6(*R*)-, and 14(*R*),15(*S*)-Epoxyeicosatrienoic Acid (EET) and Hydration Products 5(*R*),6(*R*)- and 14(*R*),15(*R*)-Dihydroxyeicosatrienoic Acid (DHET)[1]

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Recent reports[3] have elucidated an alternative mode of eicosanoid production,[4] designated the epoxygenase pathway,[5a] that

(1) Presented in part: Moustakis, C. A.; Viala, J.; Falck, J. R. "Abstracts of Papers", 189th National Meeting of the American Chemical Society, Miami Beach, FL, April–May, 1985; American Chemical Society: Washington, DC, 1985; ORGN-174.

(2) NATO postdoctoral fellow.

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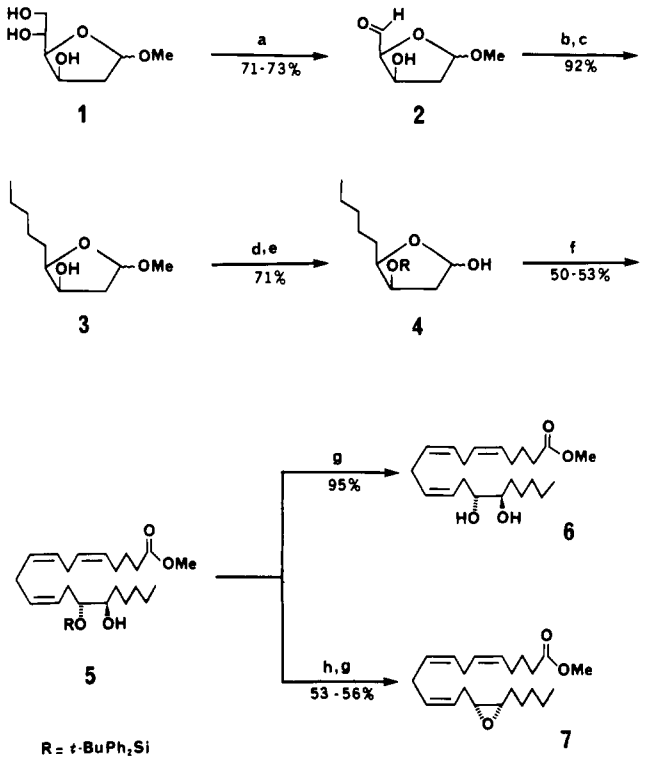
Scheme I[a]



[a] $NaIO_4$, $MeOH/H_2O$ 2:1, −15 → 0 °C, 1.5 h. [b] $BuPPh_3$, BuLi, THF/HMPA 4:1, −78 → 0 °C, 12 h. [c] 5% Pd/C, 1 atm H_2, EtOAc/MeOH 1:1, 1 h. [d] KH, $^tBuPh_2SiCl$, THF, 12 h. [e] AcOH/THF/H_2O 5:2:2, 60–65 °C, 2–2.5 h. [f] **8**, LiN $(SiMe_3)_2$, THF/HMPA, −78 → 23 °C, 12 h. [g] Bu_4NF, THF, 0 °C, 24 h. [h] TsCl, py, DMAP, CH_2Cl_2, 23 °C, 48 h.

is distinct from the cyclooxygenase and lipoxygenase branches of the arachidonate cascade. Initial metabolism is mediated by cytochrome P-450 and leads to four novel, regioisomeric *cis*-epoxyeicosatrienoic acids[6] (EETs) as well as lipoxygenase-type *Z,E* dienols[7] and $\omega/(\omega-1)$ oxygenated products.[8] The EETs exhibit significant in vitro biological activities, inter alia, stimulation of peptide hormone release,[5] mobilization of microsomal calcium,[9] and alteration of net potassium and sodium flux in the isolated rabbit kidney tubule.[10] Hydration of the EETs by epoxide hydrolases[11] results in *vic*-dihydroxyeicosatrienoic acids (DHETs) which also may have a physiological role.[5a,b] These observations, in conjunction with the in vivo detection of EETs in mammalian tissue,[12] implicate the cytochrome P-450 epoxygenase pathway as a potential participant in homeostasis. Due to the minute amounts of epoxygenase metabolites isolable from natural sources, we report herein the convergent, enantiospecific total synthesis of the title compounds utilizing an easily obtainable carbohydrate precursor.

The strategy summarized in Scheme I was calculated to provide access to both DHETs and EETs from a single chiral intermediate. Methyl furanoside (**1**), available[13] as an ~4:1 anomeric mixture from 2-deoxy-D-glucose (0.1% HCl, MeOH, 2 h; neutralization with excess $BaCO_3$), was converted to the pivotal aldehyde **2**[14] by $NaIO_4$ cleavage in 71–73% yield after chromatography. Elaboration using butyltriphenylphosphorane and catalytic reduction of the resultant olefin furnished **3** (92%) which was transformed to lactol **4** (71%) by silylation (t-$BuPh_2SiCl$, KH, THF, 12h) and hydrolysis in $AcOH/THF/H_2O$ (5:2:2, 60–65 °C, 2–2.5 h). Condensation of **4** with the ylide (3.3 equiv) derived from [10-carbomethoxydeca-(*Z,Z*)-3,6-dien-1-yl]triphenylphosphonium bromide[15] (**8**) in 4:1 THF/HMPA (−78 to 23 °C over 12 h) afforded **5** and a small amount of the corresponding 11-*E* isomer in 50–53% yield. Exposure of **5** to Bu_4NF smoothly generated (95%) methyl 14(*R*),15(*R*)-dihydroxyeicosatrienoate[16] (**6**).

Tosylation of **5**, fluoride anion desilylation with concomitant epoxide closure, gave methyl 14(*R*),15(*S*)-epoxyeicosatrienoate[16] (**7**) (64% from **5**), the predominant antipode of 14,15-EET produced by incubation of arachidonic acid with the major phenobarbital-inducible form of rat liver microsomal cytochrome P-450.[17] The stereochemical homogeneity of **7** was verified following olefin reduction (5% Pd/C, EtOAc, 1 atm H_2) by NMR analysis using chiral lanthanide shift reagents[18] under conditions which fully resolve a *d,l* mixture.

In contrast to its otherwise high enantiofacial selectivity, purified microsomal cytochrome P-450 produces 5,6-EET as a 60:40 enantiomeric mixture.[17] It was of interest, therefore, to prepare both isomers for independent pharmacological evaluation (Scheme II). Three-carbon homologation of **2** with [3-bis(isopropoxy)-propyl]triphenylphosphonium bromide[19] (**16**) and hydrogenation over 5% Pd/C furnished **9** (65%). Selective hydrolysis (0.4 M HCO_2H) of the isopropyl acetal in the presence of *m*-chloroperbenzoic acid gave the corresponding carboxylic acid. In situ esterification (Me_2SO_4, $NaHCO_3$, 23 °C, 10 h) and extractive isolation provided methyl ester **10** from which lactol **11** was obtained by acidic hydrolysis (0.5 M HCO_2H, 65 °C) in 79% yield from **9**. Union of **11** under Wittig cis-olefination conditions

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(15) Prepared in 64% overall yield from 4-[(*tert*-butyldiphenylsilyl)-oxy]-1-bromo-2-butyne by CuI (1.7 equiv) catalyzed coupling with the dianion of 5-hexynoic acid (1.7 equiv, EtMgBr) in THF/HMPA (5:1) followed by in situ esterification with $Me_2SO_4/NaHCO_3$. Sequential reduction of the resultant diyne over P-2 nickel [$NaBH_4$, $Ni(OAc)_2$, $H_2NCH_2CH_2NH_2$, EtOH, 1 atm of H_2], desilylation (20% ω/ω camphorsulfonic acid, MeOH), alcohol/bromide interchange (Ph_3P, CBr_4, CH_2Cl_2), and displacement with triphenylphosphine (CH_3CN, 85 °C) gave **8**. For an alternative sequence, see: Nicolaou, K. C.; Hernandez, P. E.; Ladduwahetty, T.; Randall, J. L.; Webber, S. E.; Li, W. S.; Petasis, N. A. *J. Org. Chem.* **1983**, *48*, 5404–5406.

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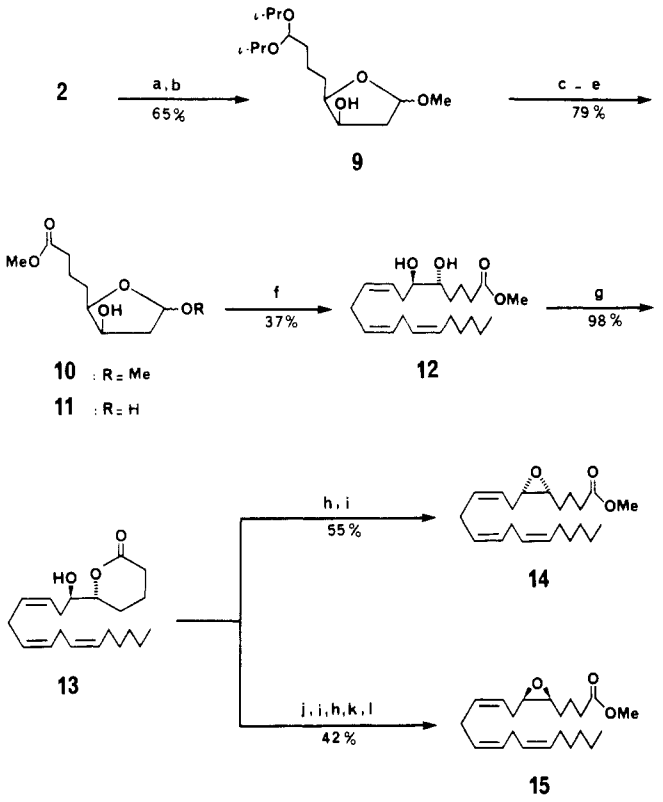
Scheme II[a]



[a] 16, BuLi, THF/HMPA 4:1, −78 → 23 °C, 12 h. [b] 5% Pd/C, 1 atm H_2, EtOH, 2 h. [c] HCO_2H, MCPBA, THF/H_2O 3:1, 35 h; Me_2S, 30 min. [d] Me_2SO_4, $NaHCO_3$, 23 °C, 10 h. [e] HCO_2H, THF/H_2O 1:1, 65 °C, 2.5 h. [f] 17, $LiN(SiMe_3)_2$, THF/HMPA, 4:1, −78 → 23 °C, 12 h; MeOH, 2 h. [g] TsOH, $PhCH_3$, 3 Å Mol. Sieves, reflux, 0.5 h. [h] TsCl, py, DMAP, CH_2Cl_2, 12–48 h. [i] Et_3N, MeOH, 12 h. [j] DHP, PPTS, CH_2Cl_2, 12 h. [k] Amberlyst H-15, MeOH, 12 h. [l] NaOMe, MeOH, 0 °C, 1 h.

(THF/HMPA 4:1, −78 to 23 °C over 12 h) with the ylide from dodeca-(*Z*,*Z*)-3,6-dien-1-yltriphenylphosphonium bromide[20] (**17**), anhydrous methanol quench (23 °C, 2 h), and chromatography secured methyl 5(*R*),6(*R*)-dihydroxyeicosatrienoate[16] (**12**) (37%). Differentiation of the diol by lactonization to **13** (98%), tosylation, and treatment with Et_3N/MeOH afforded methyl 5(*R*),6(*S*)-epoxyeicosatrienoate (**14**)[16] (55%).

Lactone **13** was also exploited for the preparation of methyl 5(*S*),6(*R*)-epoxyeicosatrienoate[16] (**15**) by the sequence: tetrahydropyranylation, lactone methanolysis, tosylation, THP removal, and epoxide closure under the influence of NaOMe (42% from **13**).

The foregoing syntheses provide ready access to sufficient quantities of the epoxygenase metabolites for pharmacological and biological testing. Investigations into their possible physiological role and metabolic fate will be reported in due course.

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Supplementary Material Available: Chromatographic, microanalytical, and spectral data for **2–7**, **9**, **10**, **12**, **14**, and **15** (2 pages). Ordering information is given on any current masthead page.

(20) Obtained in 60–65% overall yield from 2-octyn-1-ol by modification of the procedures in ref 15.

Stabilization of the Phenyl Cation by Hyperconjugation†

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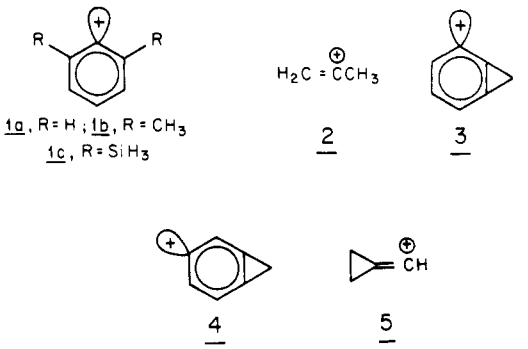
Aryl cations **1**, have attracted considerable experimental[1,2] and theoretical interest.[3,4] In solution, **1** can be generated by the decomposition of arenediazonium ions,[1] but the numerous attempts to generate these species by the solvolysis of aryl precursors have failed.[2] These failures result from the inherent low stability of the phenyl cation (**1a**), which in the gas phase is 21–25 kcal/mol less stable than the 2-propenyl cation (**2**).[5] Ab initio calculations[6,7]



give an energy difference of 27 kcal/mol at MP2/6-31G*.[8a,b] **2** is among the least stable vinyl cations that can be generated by

† Dedicated to Professor David Ginsburg on the occasion of his 65th birthday.

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