mixture was stirred at 25 °C for 15 s. It was then quenched with water and extracted with ether. The ether solution was washed with 1 N NaOH, water, and brine and dried over $MgSO_4$. The solvent was removed to give 14 mg of crude material. TLC with CH_2Cl_2 (3×) afforded **5** (5 mg), **7** (3 mg), and **6**; the latter was recycled with hexane/ether (4:1, 2×), giving 3 mg of pure material.

5:[6] UV (C_6H_{14}) λ_{max} 240, 246, 253 (sh) nm (ϵ 20 000, 21 000, 14 000); IR ν 3610, 2960, 2930, 2860, 1440, 1380, 1370, 1345, 1150, 1120, 1072 cm^{-1}; ^1H NMR (250 MHz) δ 6.07 (1 H, br s), 3.45 (1 H, dd, J = 5, 12 Hz), 2.30–1.12 (9 H, m), 1.66 (3 H, s), 1.04 (3 H, dd, J = 1.5, 7.5 Hz), 1.02 (3 H, dd, J = 1.5, 7.5 Hz), 0.90 (3 H, s).

6: mass spectrum, m/z 220.181 for $C_{15}H_{24}O$ ($M^+ - H_2O$, calcd 220.182), 205, 180, 162, 147, 133, 123, 120, 107, 105, 95, 93, 91, 79, 59; IR ν 3610, 2970, 2930, 2860, 1450, 1380, 1370, 1345, 1120 cm^{-1}; ^1H NMR (250 MHz) δ 5.55 (1 H, d, J = 3 Hz), 3.30 (1 H, dd, J = 5, 11 Hz), 2.50–1.20 (10 H, m), 1.18 (6 H, s), 1.13 (3 H, d, J = 8 Hz), 1.07 (3 H, s); ^{13}C NMR δ 148.9, 123.4, 78.4, 73.4, 45.5, 40.0, 38.6, 34.8, 30.8, 27.9, 27.1, 26.5, 22.3, 20.6, 20.0.

7: mass spectrum, m/z 220.184 for $C_{15}H_{24}O$ (M^+ – HCOOH, calcd 220.182), 205, 202, 179, 176, 163, 161, 159, 147, 145, 133, 131, 119, 117, 107, 105, 95, 93, 91, 79, 71; IR ν 3610, 2980, 2930, 2860, 1740, 1380, 1370, 1345, 1195, 1120, 1015 cm^{-1}; ^1H NMR (250 MHz) δ 8.03 (1 H, s), 5.40 (1 H, d, J = 4 Hz), 3.34 (1 H, dd, J = 4, 12 Hz), 2.50–1.12 (10 H, m), 1.47 (3 H, s), 1.45 (3 H, s), 1.12 (3 H, d, J = 8 Hz), 1.06 (3 H, s).

Reaction of 3 with *p*-Toluenesulfonic Acid: 8. To a reaction flask containing 9.0 mg of **3** in 2 mL of freshly distilled methanol was added 20 mg of *p*-toluenesulfonic acid monohydrate, and the mixture was stirred at 25 °C for 5 min. The mixture was then extracted with ether, and the ether layer washed with 5% $NaHCO_3$, water, and brine and dried over $MgSO_4$. The solvent was removed, and the crude product was purified by TLC (CH_2Cl_2/Et_2O, 95:5, 2×) to yield 3 mg of **8**: mass spectrum, m/z 237.184 for $C_{15}H_{25}O_2$ ($M^+ - CH_3$, calcd 237.185), 220, 202, 187, 145, 131, 121, 119, 115, 107, 105, 93, 91, 79, 73; IR ν 3400, 2970, 2860, 1445, 1380, 1120, 1070, 1050, 905 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 5.58 (1 H, d, J = 2.5 Hz), 3.12 (1 H, dd, J = 3, 12 Hz), 3.03 (3 H, s), 2.33–1.20 (10 H, m), 1.12 (3 H, s), 1.11 (3 H, s), 1.09 (3 H, s), 1.04 (3 H, s); ^{13}C NMR δ 147.6, 124.3, 77.3, 76.7, 48.3, 42.2, 40.2 (s), 38.8, 35.0, 30.9, 26.7, 22.6 (2C), 22.1, 20.8, 19.9.

Epoxidation of Calarene (13): 14. In a three-neck flask equipped with a dropping funnel, condenser, and thermometer was added 62.4 mg of calarene (0.26 mmol) in 1 mL of anhydrous CH_2Cl_2. *m*-Chloroperbenzoic acid (105 mg, 0.36 mmol) in 5 mL of anhydrous CH_2Cl_2 was added dropwise while maintaining the reaction temperature below 25 °C. After all the acid was added, the mixture was stirred at 25 °C overnight. The excess perbenzoic acid was destroyed by addition of 3 mL of 10% Na_2SO_3, and the benzoic acid was neutralized with 5% $NaHCO_3$. The organic layer was dried over $CaCl_2$, and the solvent was removed to give 60 mg of crude product. TLC purification with CH_2Cl_2 gave **14** as the major product (48 mg, 84%): $[\alpha]_D$ +27.5° (*c* 0.182, $CHCl_3$) (lit.[6] $(\alpha)_D$ +21.2° ($CHCl_3$)).

Acknowledgment. We thank Dr. H. H. Sun for the initial supply of organisms and Dr. Kun-Hsiung Chang of the Academia Sinica, Taipei, for subsequent collections. Special thanks to Dr. P. T. Inglefield for the 2-D ^1H NMR spectrum, Peter Demou for the 500-MHz ^1H NMR spectrum, Dr. C. E. Costello for the mass spectra, and Dr. M. R. Brennan for valuable discussions concerning these spectra. We are especially grateful to Dr. G. H. Büchi for a generous sample of calarene. We acknowledge support of the NSF Northeast Regional NMR Facility at Yale University (Grant Number CHE-7916210), the NMR Facility for Biomolecular Research at MIT (NIH Grant No. RR00995 and NSF Contract No. C-670), the Worcester Consortium NMR Facility at Clark University (NSF Grant No. DMR-8108697), and the NIH Mass Spectrometry Facility at MIT (Grant No. RR00317).

Registry No. **3**, 87332-34-1; **4**, 87261-75-4; **5**, 87261-76-5; **6**, 87261-77-6; **7**, 87261-78-7; **8**, 87279-31-0; **13**, 17334-55-3; **14**, 68926-75-0.

Synthesis of (8*E*,10*E*,12*Z*,15*Z*)-6-Oxaheneicosa-8,10,12,15-tetraenoic Acid, Secoleukotriene A_4[1]

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The discovery of the leukotrienes and the elucidation of the biosynthesis of these mediators of inflammatory and allergic disorders has presented synthetic chemists the opportunity of preparing analogues of the biochemical intermediates that may antagonize the biological effects of these intermediates or act as inhibitors of the enzymes that transform them into products further down the arachidonic acid cascade. Examples of this strategy include acetylenic[2] and allenic[3] analogues of arachidonic acid, a carbon analogue of (6*E*,8*Z*,11*Z*,14*Z*)-15(*S*)-hydroperoxyeicosa-6,8,11,14-tetraenoic acid (5-HPETE),[4] carbon,[4,5] nitrogen,[6] and sulfur[7] analogues of leukotriene A_4 (LTA_4), and the dimethylamide of leukotriene B_4 (LTB_4).[8]

The subject of this paper, secoleukotriene A_4, lacks the reactive oxirane moiety of LTA_4 and consequently cannot undergo enzymatic hydration giving LTB_4 or conjugation with glutathione giving LTC_4. However, seco-LTA_4 should have enough structural similarity to LTA_4 to bind with the enzyme and function as an inhibitor. For these reasons, the following synthesis of seco-LTA_4 (**7**, n = 4) outlined in Scheme I was undertaken.

Allyl alcohol was alkylated with trimethyl 5-bromoorthovalerate (**1**, n = 4) in the presence of aqueous KOH,[9] producing the ether **2**, n = 4, which upon mild acid treatment produced ester **3**, n = 4. Reaction of olefin **3**, n = 4, with a catalytic amount of ruthenium trichloride in the presence of excess sodium periodate[10] gave the aldehyde **4**, n = 4. Homologation of this aldehyde with (triphenylphosphoranylidene)crotonaldehyde[11] gave the dienal **5**, n = 4. Wittig olefination of **5**, n = 4 with the ylide derived from the reaction of [(*Z*)-non-3-en-1-yl]triphenylphosphonium bromide with *n*-butyllithium[12] gave (8*E*,10*E*,12*Z*,15*Z*)-methyl 6-oxaheneicosa-8,10,12,15-tetraenoate (**6**, n = 4). Decoupling of ^1H NMR spectrum of

(1) Contribution No. 650 from the Institute of Organic Chemistry, Syntex Research.

(2) For a survey, see Bailey, D. M.; Chakrin, L. W. *Annu. Rep. Med. Chem.* **1981**, *16*, 219.

(3) (a) Corey, E. J.; Kantner, S. S.; Lansbury, P. T., Jr. *Tetrahedron Lett.* **1983**, *24*, 265. (b) Patterson, J. W., Jr.; Pfister, J. R.; Wagner, P. J.; Murthy, D. V. K. *J. Org. Chem.* **1983**, *48*, 2572.

(4) Arai, Y.; Konno, M.; Shimoji, K.; Konishi, Y.; Niwa, H.; Toda, M.; Hayashi, M. *Chem. Pharm. Bull.* **1982**, *30*, 379.

(5) Nicolaou, K. C.; Petasis, N. A.; Seitz, S. P. *J. Chem. Soc., Chem. Commun.* **1981**, 1195.

(6) Zamboni, R.; Rokach, J. *Tetrahedron Lett.* **1983**, *24*, 331.

(7) Corey, E. J.; Park, H.; Barton, A.; Nii, Y. *Tetrahedron Lett.* **1980**, *21*, 4243.

(8) Showell, H. J.; Otteness, I. G.; Marfat, A.; Corey, E. J. *Biochem. Biophys. Res. Commun.* **1982**, *106*, 741.

(9) The reaction conditions used here are similar to those of Freedman and Bubois [Freedman, H. H.; Bubois, R. A. *Tetrahedron Lett.* **1975**, 3251] for the preparation of ethers from alkyl chlorides and alcohols. However, in the case of ortho esters **1**, the reaction was conveniently rapid in the absence of phase-transfer agents.

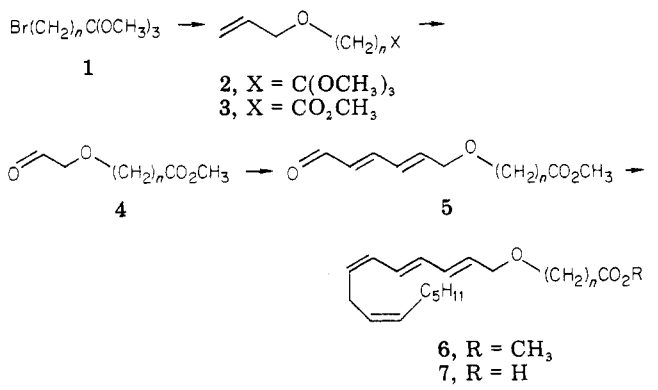
(10) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464. The conditions used here are essentially those reported for the cleavage of olefins to carboxylic acids except only 2.5 equiv of $NaIO_4$ is used. Little effort was made to improve the modest yield of **4**, but this procedure avoids the use of osmium tetraoxide, which is difficult to handle and store.

(11) (a) Ernest, I.; Main, A. J.; Menasse, R. *Tetrahedron Lett.* **1982**, *23*, 167. (b) Berenguer, M. J.; Castells, J.; Galard, R. M.; Moreno-Manas, M. *Ibid.* **1971**, 495.

(12) Corey, E. J.; Clark, D. A.; Goto, G.; Marfat, A.; Mioshowski, C.; Samuelson, B.; Hammerstrom, S. *J. Am. Chem. Soc.* **1980**, *102*, 1436.

0022-3263/83/1948-4413$01.50/0

Scheme I



tetraene **6**, $n = 4$, revealed that $J_{12,13}$ was 11 Hz in accord with the cis assignment of the stereochemistry of the newly formed double bond. The ester function of **6**, $n = 4$, was then hydrolyzed by reaction with lithium hydroxide in aqueous ethanol to give secoleukotriene A_4 (**7**, $n = 4$).

Cleavage of the 5,6 carbon–carbon bond of leukotriene A_4 has the effect of increasing the distance between the olefinic and carboxylic acid functions. Consequently, the seco compound (**7**, $n = 3$) having one less methylene unit between the ether and carboxylic acids groups were prepared. This substance was synthesized in an identical manner with the preparation of **7**, $n = 4$, beginning with trimethyl 4-bromoorthobutyrate (**1**, $n = 3$).

Compounds **7**, $n = 3$, and **4**, are currently being evaluated[13] as agents to alter arachidonic acid metabolism. Preliminary results indicate that **7**, $n = 4$, causes a decrease in the formation of LTB_4 in human polymorphonuclear leukocytes. A detailed account of the biological properties of these and related compounds will be reported elsewhere.

Experimental Section

All reactions were run under a dry nitrogen atmosphere with magnetic stirring except where mechanical stirring is specified. THF was purified by distillation from sodium/benzophenone immediately prior to use. Infrared spectra were recorded on a Pye Unicam 3-200 spectrometer as neat films. The ^1H NMR spectra were recorded in $DCCl_3$ with Me_4Si as an internal standard on a Varian EM 390 spectrometer (90 MHz) or a Bruker WM 300 spectrometer (300 MHz).

Trimethyl 6-Oxaorthonon-8-enoate (2, $n = 4$). A mixture of trimethyl 5-bromoorthovalerate[14] (**1**, $n = 4$; 9.64 g, 40 mmol), allyl alcohol (5.43 mL, 80 mmol), and 20 mL of 50% aqueous KOH was rapidly stirred with a mechanical stirrer for 2 h at 65 °C. The reaction mixture was cooled to room temperature and diluted with 50 mL of ether. The organic layer was separated, dried over K_2CO_3, and distilled to give 6.135 g (70%) of ortho ester **2**, $n = 4$: bp 75–78 °C (1 mm); IR 3080, 1640 cm^{-1} ($CH{=}CH_2$); ^1H NMR (90 MHz) δ 6.1–5.7 (m, 1, H-8), 5.35–5.0 (m, 2, H-9), 3.93 (dt, 2, $J = 6$ and 3 Hz, H-7), 3.42 (t, 2, $J = 7$ Hz, H-5), 3.23 (s, 9, OCH_3), 1.9–1.3 (m, 6, H-2–H-4).

Anal. Calcd for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.82; H, 10.26.

Methyl 6-Oxanon-8-enoate (3, $n = 4$). A mixture of ortho ester **2**, $n = 4$ (5.60 g, 25.6 mmol), 50 mL of water, 50 mL of ether, 100 mL of crushed ice, and 0.5 mL of concentrated HCl was shaken for 30 s. The acid was neutralized with $NaHCO_3$ and 100 mL of brine was added. The organic layer was separated and the aqueous layer extracted with ether (2 × 50 mL). The combined organic extracts were dried over K_2CO_3, evaporated, and distilled through a short-path apparatus to give 4.352 g (96%) of ester **3**, $n = 4$: bp 80–85 °C (2 mm): IR 1740 cm^{-1} (CO_2CH_3); ^1H NMR (90 MHz) δ 6.1–5.7 (m, 1, H-8), 5.35–5.0 (m, 2, H-9), 3.95 (dt, 2, $J = 6$ and 3 Hz, H-7), 3.65 (s, 3, CH_3), 3.43 (t, 2, $J = 7$ Hz, H-5), 2.32 (t, 2, $J = 7$ Hz, H-2), 1.9–1.5 (m, 4, H-3 and H-4).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.63; H, 9.41.

Methyl 6-Oxa-8-oxooctanoate (4, $n = 4$). A mixture of 50 mL of water, 20 mL of acetonitrile, 20 mL of CCl_4, and 5.26 g (25 mmol) of $NaIO_4$ was cooled on ice and treated with 1.58 g (9.2 mmol) of allylic ether **4**, $n = 4$, and 100 mg (0.38 mmol) of $RhCl_3 \cdot 3H_2O$. After stirring 2.5 h at 0 °C, the reaction mixture was diluted with 100 mL of brine and extracted with ethyl acetate (4 × 75 mL). The extracts were dried over Na_2SO_4, evaporated, and chromatographed on silica gel (eluting with 25% ethyl acetate/hexane). The major product was collected and evaporatively distilled to give 782 mg (49%) of aldehyde **4**, $n = 4$: bp 110 °C (0.1 mm); IR 1730 cm^{-1} (CHO and CO_2 CH_3); ^1H NMR (300 MHz) δ 9.73 (t, 1, $J = 0.7$ Hz, H-8), 4.08 (d, 2, $J = 0.7$ Hz, H-7), 3.68 (s, 3, CH_3), 3.56 (t, 2, $J = 6$ Hz, H-5), 2.37 (t, 2, $J = 7$ Hz, H-2), 1.8–1.6 (m, 4, H-3 and H-4).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.23; H, 8.12.

(8*E*,10*E*)-Methyl 6-Oxa-12-oxododeca-8,10-dienoate (5, $n = 4$). To a solution of 1.40 g (4.2 mmol) of (triphenylphosphoranylidene)crotonaldehyde in 15 mL of CH_2Cl_2 was added a solution of 600 mg (3.4 mmol) of aldehyde **4**, $n = 4$, in 10 mL of CH_2Cl_2 over a 25-min period. The reaction mixture was stirred at room temperature for 90 min and then chromatographed without workup on silica gel (eluting with 20% ethyl acetate/toluene). This gave a mixture of two products with similar R_f values, which were dissolved in 10 mL of CH_2Cl_2 and treated at room temperature with 3 mg of I_2 for 2 h. The reaction mixture was diluted with 50 mL of CH_2Cl_2, washed with aqueous sodium thiosulfate and brine, and dried over K_2CO_3. Silica gel chromatography then gave 327 mg of dienal **5**, $n = 4$: IR 1730, 1680, 1640, 1600 cm^{-1} (dienone); UV 267 nm (ϵ 18 200); ^1H NMR (300 MHz) δ 9.58 (d, 1, $J = 8$ Hz, H-12), 7.13 (dd, 1, $J = 12$ and 15 Hz, H-10), 6.55 (ddt, 1, $J = 15$, 12, and 2 Hz, H-9), 6.30 (dt, 1, $J = 15$ and 5 Hz, H-8), 6.17 (dd, 1, $J = 15$ and 8 Hz, H-11), 4.13 (dd, 1, $J = 5$ and 2 Hz, H-7), 3.68 (s, 3, CH_3), 3.50 (t, 2, $J = 6$ Hz, H-5), 2.37 (t, 2, $J = 7$ Hz, H-2), 1.8–1.6 (m, 4, H-3 and H-4).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.89; H, 7.99.

(8*E*,10*E*,12*Z*,15*Z*)-Methyl 6-Oxaheneicosa-8,10,12,15-tetraenoate (6, $n = 4$). A mixture of [(*Z*)-non-3-en-1-yl]triphenylphosphonium bromide (500 mg, 1.17 mmol) and 35 mL of THF was heated briefly to 50 °C to effect dissolution and then cooled to −70 °C. A 0.85-mL sample of 1.4 N *n*-butyllithium was added and the reaction mixture was stirred 30 min at −70 °C. After a solution of 2 mL of HMPA in 3 mL of THF was added, the dienal **5**, $n = 4$ (250 mg, 1.10 mmol in 3 mL of THF), was added and the reaction mixture kept at −70 °C for 10 min. After warming to −40 °C for 5 min, the reaction mixture was poured into aqueous $NaHCO_3$ and extracted with ether. The organic extract was dried over K_2CO_3, evaporated, and chromatographed on silica gel (60 g, eluting with 10% ether/hexane) to give 234 mg (64%) of tetraene **6**, $n = 4$: IR 1740 cm^{-1} (CO_2CH_3); UV 272, 283 nm (ϵ 37 400 and 29 700); ^1H NMR (300 MHz) δ 6.52 (dd, 1, $J = 14$ and 12 Hz, H-11), 6.32 (dd, 1, $J = 14$ and 11 Hz, H-9), 6.21 (dd, 1, $J = 14$ and 11 Hz, H-10), 6.04 (dd, 1, $J = 12$ and 11 Hz, H-12), 5.78 (dt, 1, $J = 14$ and 6 Hz, H-8), 5.5–5.3 (m, 3, H-13, H-15 and H-16), 4.01 (d, 2, $J = 6$ Hz, H-7), 3.68 (s, 3, CO_2CH_3), 3.44 (t, 2, $J = 7$ Hz, H-5), 2.94 (t, 2, $J = 7$ Hz, H-14), 2.35 (t, 2, $J = 7$ Hz, H-2), 2.06 (dt, 2, $J = 7$ and 7 Hz, H-17), 1.8–1.6 (m, 4, H-3 and H-4), 1.4–1.25 (m, 6, H-18, H-19, H-20), 0.89 (t, 3, $J = 7$ Hz, H-21).

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.26. Found: C, 75.26; H, 10.22.

(8*E*,10*E*,12*Z*,15*Z*)-6-Oxaheneicosa-8,10,12,15-tetraenoic Acid (7, $n = 4$). Ester **6**, $n = 4$ (156 mg, 0.46 mmol in 1 mL of ethanol), was added to a solution of LiOH (80 mg, 1.9 mmol) in 2 mL of 1:1 water/ethanol. The reaction mixture was stirred at room temperature for 40 min. After cooling on ice, the reaction mixture was acidified to pH 2 with 10% HCl, diluted with 10 mL of brine, and extracted with ethyl acetate (2 × 20 mL). Silica

(13) For a description of this assay, see Pfister, J. R.; Murthy, D. V. K. *J. Med. Chem.* **1983**, *26*, 1099.

(14) The ortho esters **1**, $n = 3$ and 4, were prepared from 4-bromobutyronitrile and 5-bromovaleronitrile by the method of McElvain and Aldridge: McElvain, S. M.; Aldridge, C. L. *J. Am. Chem. Soc.* **1953**, *75*, 3987.

chromatography (eluting with 10% ether/1% acetic acid/hexane) gave 114 mg (76%) of the acid **7**, $n = 4$: IR 1710 cm^{-1} (CO_2H); UV 272, 283 nm (ϵ 47 700 and 37 400); ^1H NMR (300 MHz) was identical with the spectrum of **6**, $n = 4$, except the CO_2CH_3 signal was missing and the triplet for H-2 was at 2.39 ppm.

Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 74.68; H, 10.21.

Registry No. **1** ($n = 3$), 55444-67-2; **1** ($n = 4$), 87307-20-8; **2** ($n = 4$), 87307-21-9; **3** ($n = 4$), 87307-22-0; **4** ($n = 4$), 87307-23-1; **5** ($n = 4$), 87307-24-2; **6** ($n = 4$), 87307-25-3; **7** ($n = 3$), 87307-26-4; **7** ($n = 4$), 87307-27-5.

^{15}N Nuclear Magnetic Resonance Spectroscopy of 1-Phenyl-3,3-pentamethylenetriazenes

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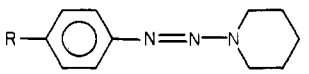
The π-conjugated nitrogen system of 1-phenyl-3,3-dialkyltriazenes is extremely stable against loss of nitrogen, and on reaction with acidic reagents the triazene system is converted to aryldiazonium salts. These combined properties of aryltriazenes are largely responsible for the increased use of aryltriazenes in synthetic and radiopharmaceutical chemistry.[1-5] The value of aryltriazenes in preparative chemistry and their interesting linear π-conjugated nitrogen system led us to investigate in some detail the ^{15}N nuclear magnetic resonance spectroscopy of the 1-phenyl-3,3-pentamethylenetriazene (**1**) system.

The use of ^{15}N nuclear magnetic resonance spectroscopy as a tool for studying the electronic structure of nitrogenous systems is well-known.[6] In 1976, Pregosin et al. made a preliminary study of three aryltriazene systems, using both ^{15}N and ^{13}C NMR spectroscopy, and concluded that aryltriazenes have dipolar character.[7] We now report a detailed study of the effect of polar substituents on the ^{15}N NMR chemical shifts of **1** and discuss the electronic structure of the aryltriazenes.



1

The ^{15}N NMR spectra of **1**, as exemplified by the spectrum of 1-phenyl-3,3-pentamethylenetriazene shown in Figure 1, are relatively simple, showing three distinct chemical shifts. The signal at δ −16.98 is assigned to N(1) by comparison with the spectrum of a sample enriched with N-15 in the 1-position. The signal at δ −206.33 is assigned to N(3) because it is sensitive to the type of secondary amino substituent. Thus, a change from a pentamethylenetriazene to a (diethylamino)triazene causes a chemical shift change of 4.5 ppm at N(3), while the other nitrogen resonances are little affected. The resonance at δ 73.54 is the only remaining signal, and it is therefore assigned to N(2).

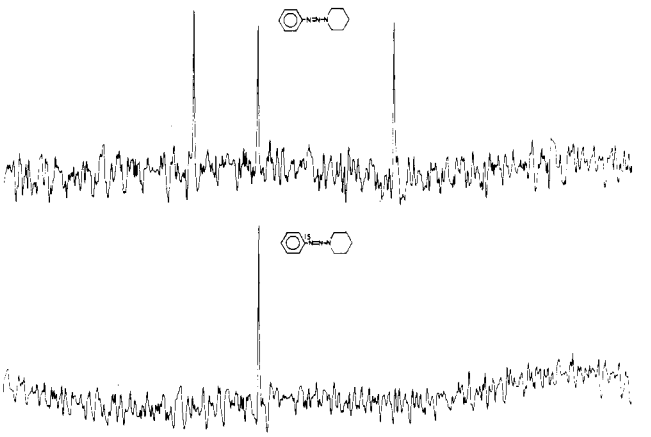
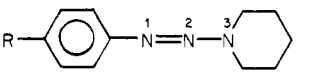


Figure 1. Upper spectrum: ^{15}N NMR spectrum of **1** at natural abundance (40% w/v, 43 000 scans). Lower spectrum: ^{15}N NMR spectrum of **1** with ^{15}N enrichment at N(1) (95% enrichment, 5% w/v, 23 000 scans).

Table I. ^{15}N NMR Chemical Shifts[a]

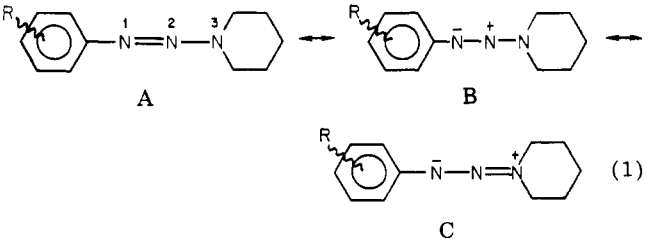


R	σ[b]	$\delta_{N(1)}$	$\delta_{N(2)}$	$\delta_{N(3)}$
CH_3O	−0.268	−12.90	72.25	−208.81
CH_3CH_2O	−0.244	−13.33	72.4	−209.67
CH3	−0.17	−13.76	73.34	−207.52
H	0	−16.98	73.54	−206.23
F	0.062	−18.49	73.55	−206.45
Cl	0.227	−21.72	73.98	−204.30
Br	0.232	−21.29	74.41	−203.87
CH_3CO	0.50	−26.45	75.27	−200.00
CN	0.66	−30.11	76.17	−197.2
NO_2	0.78	−32.90	76.56	−194.62

[a] Relative to external $NH_4{}^{15}NO_3$. Positive numbers are ppm dowfield from the standard. [b] Values taken from Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 145.

The occurrence of N(3) upfield from N(1) and N(2) is consistent with the amine-like character of N(3). However, the triazene amine resonance of N(3) is approximately 50-ppm downfield from an isolated amine resonance. In addition, the azo resonances of N(1) and N(2) of the triazene are approximately 45-ppm upfield from that observed for isolated azo systems. These results qualitatively show the presence of a π-conjugated interaction for the entire triazene system.

The effect of the polar substituents on the nitrogen chemical shifts are discussed with reference to structures A–C in eq 1.



A B

C (1)

All of the nitrogen chemical shifts give an exceptionally good linear correlation with the polar Hammett σ values as shown in Figure 2 and Table I. N(1) shows the largest

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