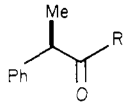

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size of R increases.[10] When a Lewis acid coordinates with an aldehyde, it probably occupies the position syn to the hydrogen. Thus, a nucleophile may be forced to approach the carbonyl plane in a more perpendicular fashion, resulting in greater stereoselection (Figure 2).

It should be noted that Danishefsky and co-workers have also observed high diastereofacial preferences in Lewis acid mediated cycloadditions of silyloxydienes to chiral aldehydes, including aldehyde **1a**.[11] Evidence has recently been developed that, at least under some conditions, the latter process proceeds by a two-step mechanism involving an initial aldol-type addition of the enolsilane to the Lewis acid coordinated aldehyde. An explanation similar to that presented in Figures 1 and 2 has also been advanced by Danishefsky.[11] Further experiments aimed at elucidating the nature of the transition state in the Mukaiyama aldol reaction are in progress.

Acknowledgment. This work was supported by an NIH Postdoctoral Fellowship to L.A.F. (GM08004) and by a research grant from the NIH (AI15027). C.H.H. acknowledges several fruitful discussions with Professors Ed Burgess and Charles Liotta, of the Georgia Institute of Technology, on the subject of this paper.

Supplementary Material Available: Experimental methods and analytical data for the compounds used (11 pages). Ordering information is given on any current masthead page.

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Convenient Direct Synthesis of $(SN)_x$ Films from S_4N_4 at Lower Temperatures

M. W. R. Witt, W. I. Bailey, Jr., and R. J. Lagow*

Department of Chemistry, The University of Texas
Austin, Texas 78712

Received July 29, 1982

The outstanding conducting properties of both $(SN)_x$ and halogenated $(SN)_x$ have been of widespread interest in recent years.[1] All previously reported syntheses of $(SN)_x$ require complicated chemical reactions[2] or the dangerous[3] pyrolysis of S_4N_4[1] or substitutes[4] over silver or quartz wool at 200 °C to form S_2N_2, which topochemically polymerizes at room temperature.

We report here a synthesis of $(SN)_x$ that excludes all these disadvantages.[5] Earlier work has shown[6] that a radio frequency glow discharge is a convenient source for the generation of radicals by homolytic cleavage of small molecules in the gas phase, which were reacted with metal atoms to form a wide variety of σ-bonded compounds.

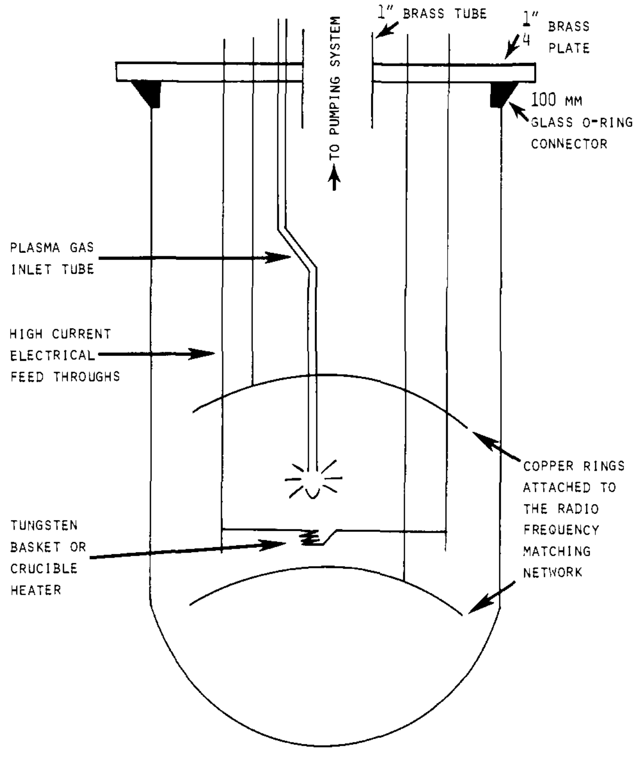

Figure 1.

In a similar manner, S_4N_4 can be sublimed at 70–80 °C into a helium plasma by using the reactor shown in Figure 1. The S_4N_4 is placed in a quartz crucible and is heated resistively by using a tungsten crucible heater. The helium is slowly metered into the reactor through the plasma gas inlet tube. By attaching the two power leads from a Tegal Corp. 100-W radio frequency power supply to two internal copper rings, the radio frequency power can be capacitively coupled to the plasma gas. The Pyrex reactor vessel is submerged in liquid nitrogen, which rapidly condenses the products as they are formed.

A 10-MHz radio frequency discharge at a power level of 40 W yields a greenish-blue film with metallic lustre on the reactor walls:

$$S_4N_4(g) \xrightarrow{rf} (SN)_x(s)$$

This material contains a mixture of $(SN)_x$ and unreacted S_4N_4. The latter was separated by washing with CH_2Cl_2 to yield pure $(SN)_x$. Thus, 0.5 g of S_4N_4 can be converted in a 3-h period to yield ca. 0.25 g of $(SN)_x$, which was identified[7] by chemical properties, IR spectra,[8] elemental analysis,[9] and powder pattern X-ray data.[10] A minor amount of volatile products condensed in a trap were identified as S_4N_2[11] and oligomers of SN, which slowly converted into $(SN)_x$.[12]

Our initial attempts at direct fluorination of $(SN)_x$ to yield a fluorinated polymer were unsuccessful. Instead, the products were identical with those obtained by direct fluorination of S_4N_4.[13] Since the halogenated $(SN)_2$ contains Br_3- and ICl_2- units be-

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(8) Infrared spectrum (KBr pellet) 1400 (m), 1225 (m), 1010 (w), 930 (w), 690 (w), 600 (w) cm^{-1}.

(9) Anal. Calcd: N, 30.4. Found: N, 27.3.

(10) Cu Kα radiation, unfiltered, 2 *r*, *I* (estimated intensity) 23.7, 1; 26.4, 8; 29.9, 3; 32.8, 9; 35.4, 9; 40.7, 10; 43.8, 2; 47.0, 10; 52.9, 10; 56.0, 3; 66.0, 2; 68.2, (1); 72.7, (1); 77.2, 1; 85.7, 1; 94.5, (1).

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tween the polymer chains,[14] the expected bonding as well as chemical properties of a fluorinated $(SN)_x$ would have been quite different.

Acknowledgment. This work was supported by a NATO Grant through the Deutsche Akademische Austauschdienst to M.W. R.W. and a collaborative NATO Grant (198.80) to R.J.L. and H. W. Roesky.

Registry No. S_4N_4 homopolymer, 58813-83-5.

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Host Recognition in Parasitic Angiosperms: Use of Correlation Spectroscopy To Identify Long-Range Coupling in an Haustorial Inducer

John C. Steffens, James L. Roark, David G. Lynn,* and James L. Riopel

Departments of Chemistry and Biology
University of Virginia, Charlottesville, Virginia 22901

Received October 25, 1982

Simple proximity relationships and relative stereochemistries of substituents in natural and synthetic organic molecules are routinely deduced from ^1H NMR coupling constants. The verification of distant intramolecular relationships frequently requires the measurement of nuclear Overhauser enhancements,[1,2] T_1 relaxation times,[2] or lanthanide-induced chemical shift changes.[3] A recent report by Bax et al.[4] showed that small couplings could be observed by proton correlation spectroscopy (COSY). The intriguing possibility of routinely identifying through-bond proximities over five and six atoms has motivated our exploration of correlation spectroscopy.[5] We now describe the structure assignment of a xenognostic triterpene isolated from a host of the parasitic angiosperm *Agalinis purpurea*, by the identification of long-range couplings.

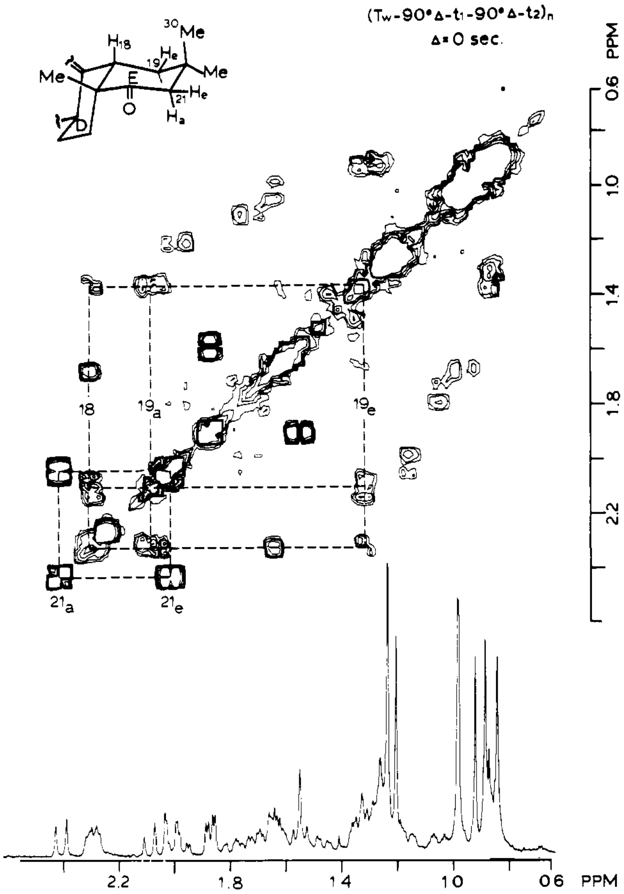
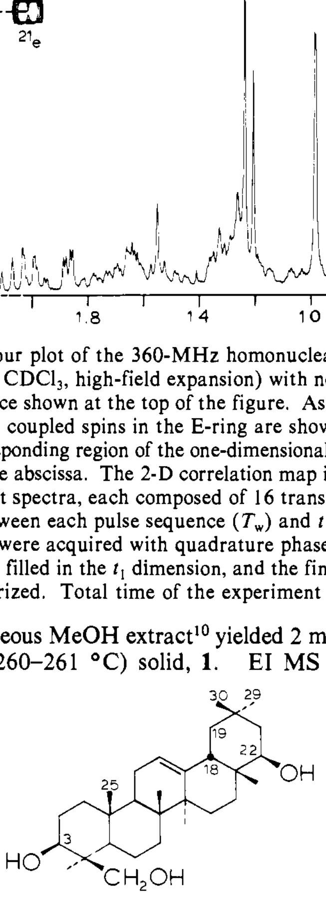


Figure 1. Contour plot of the 360-MHz homonuclear spin correlation map of **3** (2 mg, $CDCl_3$, high-field expansion) with no delay inserted in the pulse sequence shown at the top of the figure. Assignments of cross peaks indicating coupled spins in the E-ring are shown with the dotted lines. The corresponding region of the one-dimensional ^1H NMR spectra is provided on the abscissa. The 2-D correlation map is composed of 128 × 512 data point spectra, each composed of 16 transients. A 4-s delay was allowed between each pulse sequence (T_w) and t_1 was incremented by 554 s. Data were acquired with quadrature phase detection in both dimensions, zero filled in the t_1 dimension, and the final 256 × 256 data set was symmetrized. Total time of the experiment was 2.31 h.

Host recognition by the parasitic plant *Agalinis purpurea* (Scrophulariaceae) is mediated through the differentiation of a specialized attachment organ termed an haustorium.[6] The differentiation of the haustorium in *Agalinis* is dependent on specific molecular signals produced in the host root, exuded, and thereby recognized by the parasite. Although we have identified structurally specific molecules that induce haustorial differentiation,[7-9] these compounds were not derived from a natural host. For that reason, the fractionation of 400 g of 3-month-old vermiculite-grown *Lespedeza sericea* (Leguminosae) roots has been directed by haustorial-inducing activity in axenic cultures of *A. purpurea*.[7] Droplet countercurrent chromatography (7:13:8 $CHCl_3/CH_3OH/H_2O$) and repeated flash chromatography (SiO_2) of the 50% aqueous MeOH extract[10] yielded 2 mg of a crystalline (MeOH, mp 260–261 °C) solid, **1**. EI MS (70 eV) gave a molecular ion at m/z 458.3757, $C_{30}H_{50}O_3$ (calcd 458.3760),[11] and the major fragment ions at m/z 234 and 224 suggested a retro-Diels–Alder fragmentation of an olean-12-ene triterpene bearing two oxygen atoms on the A–B ring fragment.[12] Seven quaternary methyl singlets in ^1H NMR (360 MHz, acetone-d_6) and a single olefinic proton (δ 5.5 (t, J = 2.5 Hz)) supported the oleanene assignment. Three hydroxyl substituents were identified with deuterium-exchange negative ion CI MS (EtOD, N_2O)[13] by the



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