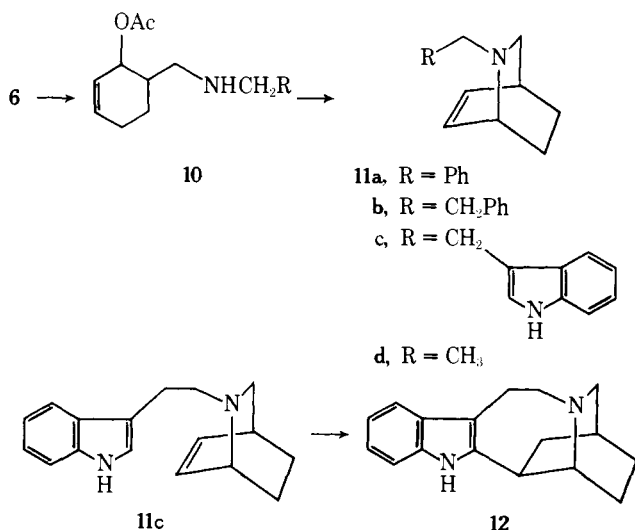


Scheme III. Synthesis of Isoquinuclidine System. Synthesis of Desethylbogamine



10a and **b**.⁸ Cyclization (catalytic amount of $(\text{Ph}_3\text{P})_4\text{Pd}$, $(\text{C}_2\text{H}_5)_3\text{N}$, CH_3CN , 70°C , 1.5 h) gave the desired isoquinuclidines **11a** and **b**⁸ in 65 and 56% yields, respectively. The structures were confirmed spectroscopically and by elemental composition. The NMR spectra match that reported for the *N*-methyl derivative **10d**¹⁴ indicating the syn relationship of the *N*-alkyl substituent and the double bond. Such a stereochemistry is necessary for the synthesis of the iboga system and led to a facile approach to desethylbogamine. The success of this net $\text{S}_{\text{N}}2'$ cyclization suggests the intermediacy of the π -allyl complexes and that ring strain determines the regiochemistry.

Repetition of the above reductive amination utilizing tryptamine gave in 68% yield the desired amino acetate **10c** as a viscous oil which upon cyclization in the standard way gave isoquinuclidine **11c**^{8,11} (mp $118\text{--}120^\circ\text{C}$ from acetonitrile) in 60% yield. Again, the similarity of the NMR spectrum for the isoquinuclidine nucleus to those of **10a-c** confirms the syn relationship of the tryptyl unit and the double bond. The final cyclization was also envisioned to utilize palladium catalysis to achieve chemospecificity in the presence of the basic nitrogen. Treatment of the lithio derivative with mercuric chloride followed by palladium chloride in THF and quenching with sodium borohydride gave desethylbogamine, mp $182\text{--}184^\circ\text{C}$, identical by NMR, MS, and TLC with an authentic sample.⁶ This cyclization, modeled after the Heck arylation reaction,¹⁵ is envisioned to involve the cis addition of an organopalladium intermediate to the double bond followed by reductive cleavage of the C-Pd bond. These results demonstrate the feasibility and potential utility in organic synthesis of palladium catalyzed cyclizations¹⁶ that proceed by $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}2'$ substitution with net retention of configuration.

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ethylamine leads predominantly to the *cis* allylic amine; whereas, the reaction of the *trans* allylic acetate with diethylamine leads predominantly to the *trans* allylic amine. Control experiments show that in the absence of the palladium catalysts no substitution and/or cyclization products are obtained.

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Opto-Galvanic Detection of Species in Flames

Sir:

An electrical signal, resulting directly from discreet optical absorptions in atomic vapors,¹⁻⁶ has been observed in atmospheric pressure analytical flames. Specifically, if the current from a constant voltage source is passed through the flame, the current is found to change when the flame is irradiated by intense monochromatic radiation (laser) corresponding to an absorption of a species present in the flame. This change in current is easily detected by standard electrical measurement techniques and can be used for spectroscopy, analytical determinations, and combustion research. In many respects, the technique corresponds to the generation of fluorescence excitation spectra with the important difference that no optical measurements are necessary to detect the absorption process. Consequently, problems associated with the measurement of weak optical signals, such as collection efficiency and scattered excitation light, are no longer important. As an example of the analytical application of this technique, the quantitative analysis of sodium in a flame is described.

The apparatus used for the detection of sodium in an air-C₂H₂ flame is shown in Figure 1. The flame was irradiated by a commercial, CW tunable dye laser chopped at 2 kHz. The bandwidth of the laser was approximately 0.003 nm and the wavelength could be fine-tuned over a range of 0.05 nm by tilting a 0.5-mm thick etalon placed in the laser cavity. The

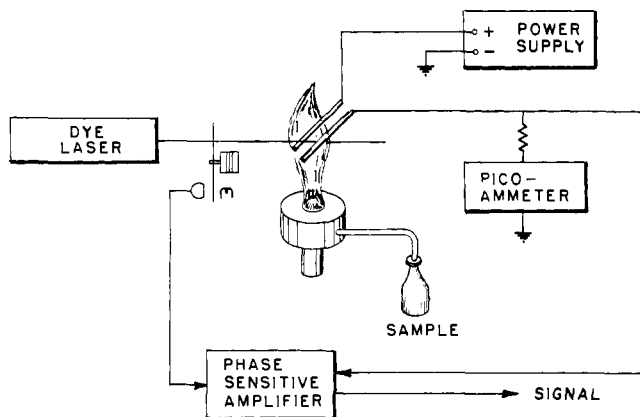


Figure 1. Apparatus for the detection of the opto-galvanic effect in flames.

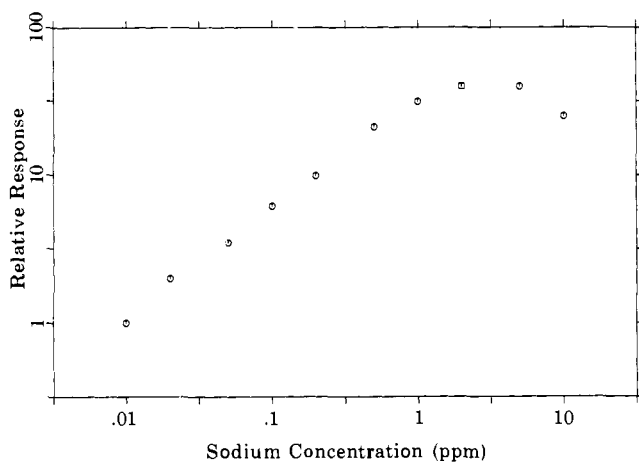


Figure 2. Log-log plot of relative signal from the 589.0-nm transition as a function of sodium concentration.

laser wavelength could be repetitively and reproducibly scanned by rotating the etalon with an oscillatory torsion motor. The laser power was approximately 50 mW, yielding a spectral irradiance of about $500 \text{ W cm}^{-2} \text{ nm}^{-1}$. The ac current component induced by the chopped laser was detected by a phase-sensitive detector and displayed as a function of wavelength on a multichannel analyzer. A premix burner with a capillary burner head was used with a fuel rich air- C_2H_2 flame. The electrodes were thoriated tungsten welding rods, 1 mm in diameter and placed 4 mm apart.

Current changes due to the absorbed light as large as 2% (independent of chopping frequency, from 0–2 kHz) were observed when a solution containing 10 ppm sodium was aspirated into the flame. A log-log plot of the opto-galvanic signal from the 589.0-nm transition vs. sodium concentration is shown in Figure 2. The analytical curve is smooth and slightly less than linear before the onset of "self-reversal". The small nonlinearity observed could be an inherent property of the effect or it may have been caused by electrode configuration, electrode erosion, and effects of large sodium concen-

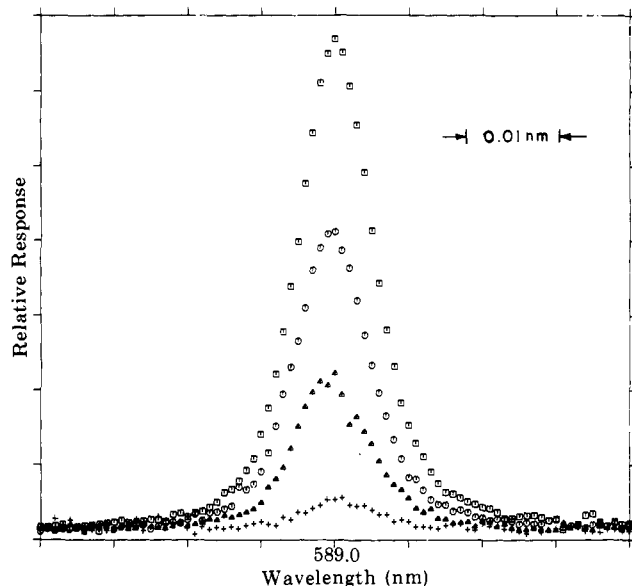


Figure 3. Opto-galvanic signal as a function of wavelength ($\sim 0.05 \text{ nm}$ total scan) for several concentrations of sodium: \square 10 ppb, \circ 5 ppb, \triangle 2 ppb, + blank.

trations on the flame conductivity. Data for concentrations of 10, 5, and 2 ppb are shown in Figure 3. The signal to noise ratio for the 2-ppb data is greater than 20.

Limitations of the laser utilized have restricted observations in the flame thus far to both sodium D lines in H_2 -air and C_2H_2 -air flames and to the barium 553.5-nm resonance transition in C_2H_2 -air and C_2H_2 - N_2O flames. The potential applicability of the technique to many additional elements is inferred from companion experiments in hollow cathode lamps⁶ and from the assumption that the effect is a resonance photoenhancement of thermal ionization occurring in the flame.

Further experiments to more completely characterize the effect are in progress.

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