

Reaction Ia has been reported,¹ and methyl-di-phenylsilyllithium, prepared from the disilane,⁸ was added to an ether solution of the (+)-chlorosilane and gave the (-)-disilane (*Anal.* Calcd.: C, 77.25; H, 8.30; Si, 14.45. Found: C, 77.40; H, 8.21; Si, 14.45) as a clear colorless liquid having $[\alpha]_D -5.03^\circ$ (*c* 6.3, benzene), in 82% yield after purification by chromatography over silica gel. In reaction sequence 2, a solution of (-)-disilane in tetrahydrofuran was added all at once to shiny lithium foil at 0° in an atmosphere of dry oxygen-free nitrogen. After 6 hr. of stirring the reactants, the solution of R_3Si^*Li in THF was syringed out of the flask and into a mixture of ether and dilute hydrochloric acid. Fractional distillation gave 50–60% yields of optically active neopentylphenylmethylsilane, R_3Si^*H .

Acknowledgment. We thank Dow Corning Corporation for continued generous support.

(8) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

Leo H. Sommer, Richard Mason

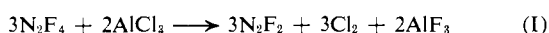
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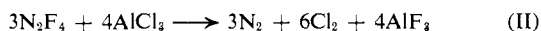
Preparation of *trans*-Difluorodiazine

Sir:

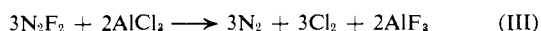
Pure *trans*-difluorodiazine can readily be prepared in about 45% yield from commercially available tetrafluorohydrazine and aluminum chloride.



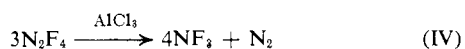
Reaction I is invariably accompanied by the formation of elementary nitrogen which accounts for the bulk of the N_2F_4 used.



The product N_2F_2 is also relatively slowly reduced by $AlCl_3$ to give elementary nitrogen and chlorine.



An additional undesirable reaction which may occur is the disproportionation of N_2F_4 to give nitrogen and NF_3 .



Reaction IV proceeds almost quantitatively at room temperature in the presence of trace quantities of $AlCl_3$.

Fortunately, both reactions III and IV can be inhibited effectively by adjusting conditions of temperature and pressure, respectively. Reaction III is extremely slow at -80° while reactions I, II, and IV are still quite rapid. The rate of disproportionation of N_2F_4 in the presence of $AlCl_3$ (reaction IV) is strongly pressure dependent, becoming almost negligible at pressures below 20 mm.

Consistent yields of 45–48% *trans*- N_2F_2 have been obtained from both batch and flow reactions involving

excess $AlCl_3$ and N_2F_4 at 15–20 mm. and -80° with contact times ranging from 0.5 to 5 min. Because of the necessarily low pressures, flow systems are strongly recommended.

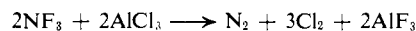
A convenient reactor can be prepared by subliming anhydrous $AlCl_3$ (15–20 g. for 30–50 mmoles of N_2F_4) onto the side-arm walls of a conventional Pyrex U-tube (16 mm. o.d.) by heating the material in the bottom of the vessel with a bunsen burner. It is necessary to activate the $AlCl_3$ before use by keeping it in contact with a small quantity of N_2F_4 at room temperature for 30 min. *Caution.* Do not use glass wool in the reaction tube as it may ignite.

The product is purified by washing with aqueous caustic soda followed by trap-to-trap vacuum distillation. Any unchanged N_2F_4 in the product can be destroyed by shaking it with water in the presence of elementary oxygen and a trace of nitric oxide. Concentrated nitric acid has also been used to remove N_2F_4 but this reagent should be avoided because of the danger of possible detonation. Samples of *trans*- N_2F_2 prepared in 48% yield in this laboratory contained approximately 0.2% NF_3 as the only impurity detectable in the infrared spectrum.

Observations made during the investigation of the above reactions indicate that at least two unstable solid NF-containing compounds are also formed in small amounts. Below -132° the activated $AlCl_3$ described above absorbs some N_2F_4 which cannot be pumped off. On warming, the solid liberates a mixture of N_2F_4 , *trans*- N_2F_2 , N_2 , and Cl_2 . Similarly, the reaction of N_2F_4 with $AlCl_3$ at -80° yields not only gaseous products but also a solid which slowly decomposes to give N_2 and Cl_2 at this temperature. In the presence of traces of moisture, N_2O is also formed in small amounts.

Additional work in this area is now in progress, including the study of reactions involving other metal salts and the nitrogen fluorides. Preliminary results indicate that $FeCl_3$ is similar to $AlCl_3$ in its action on N_2F_4 but the iron compound is considerably less reactive.

Contrary to an early report¹ by Ruff, NF_3 is also readily reduced to nitrogen by $AlCl_3$ at 70° .



Acknowledgment. This research was supported by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham) under Contract No. DA-31-124-ARO(D)-76

(1) O. Ruff, *Z. anorg. allgem. chem.*, **197**, 283 (1931).

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Electronic Spectra and Photochemistry of Adsorbed Organic Molecules. I. Spectra of Ketones on Silica Gel

Sir:

We have observed that silica gel-cyclohexane and silica gel-benzene matrices, if of sufficiently short path length, are highly transparent in the near-ultraviolet

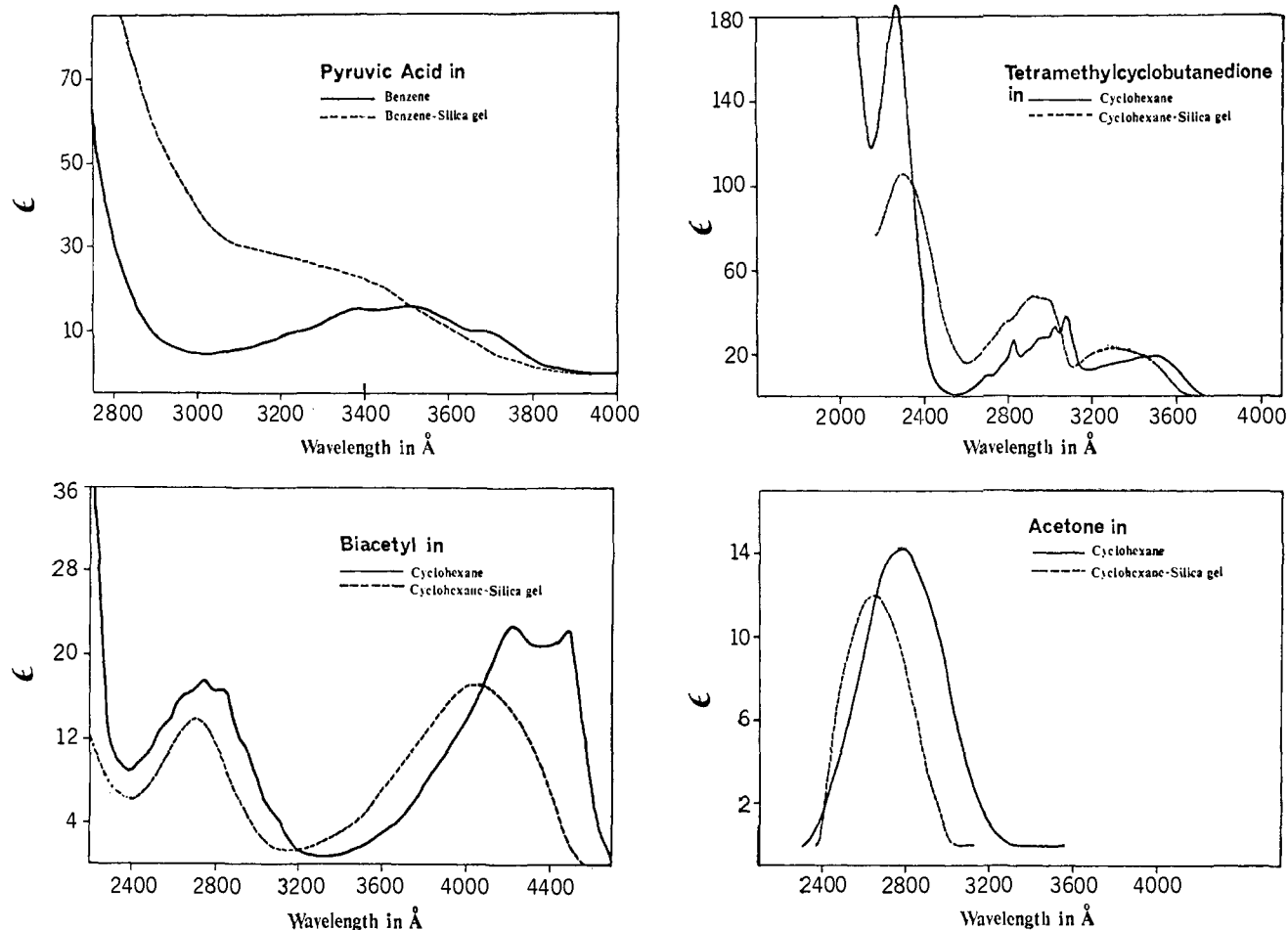


Figure 1.

and provide an excellent medium for the determination of quite well-resolved electronic absorption spectra of organic molecules. The remarkable shifts observed, when compared with cyclohexane, benzene, or ethanol alone as solvents, should help to elucidate not only the nature of the physical adsorption process, but also the nature and configuration of the excited states of the organic molecules studied.¹

Figures 1 and 2 illustrate the kind of resolution obtainable and the spectral shifts observed for the six compounds examined in pure cyclohexane (or benzene in the case of pyruvic acid) and in the solvent-silica gel slurry.⁵ In the cases of benzophenone and benzil,

(1) In the past 25 years there have been a few, mostly qualitative observations of spectral changes in molecules adsorbed on silica gel and silicic acid. For references, see Robin and Trueblood.² Subsequent to the latter reference, Kotov³ has compared the spectrum of benzaldehyde in ethanol to that on silica gel, and Okuda⁴ has recorded the spectrum of benzene vapor adsorbed on silica gel, observing a slight red shift in the lowest energy transition. The most extensive discussion to date on the subject is Robin and Trueblood's² account of the spectra of a number of aromatic molecules in a silicic acid-cyclohexane slurry (no ketones were studied). The medium, being quite acidic, gave rise to pronounced blue shifts in several anilines and nitro compounds. Red shifts in the $\pi-\pi^*$ transitions of these and the other compounds studied were generally small.

(2) M. Robin and K. N. Trueblood, *J. Am. Chem. Soc.*, **79**, 5138 (1957).

(3) E. I. Kotov, *Optika i Spektroskopiya*, **3**, 368 (1957).

(4) M. Okuda, *Nippon Kagaku Zasshi*, **82**, 1118 (1961).

(5) All spectra were recorded on a Cary 14 spectrophotometer. Cells were standard quartz Beckman cells except that the path length was 0.1 cm. The procedure for filling the cells was as follows: The ketone, of known concentration in the appropriate solvent (usually cyclohexane),

spectra in ethanol were also recorded. Spectra were entirely reproducible with respect to λ_{\max} , and reasonably so with respect to ϵ .

A theoretical discussion will be presented at a later time; however, in most cases one can generalize that n,π^* excited states are less polar than the ground-state molecule, and that the reverse is true for π,π^* states. Activated silica gel contains highly polar protonated sites which should serve to bind nonbonding electrons on carbonyl oxygen. Excitation of such "bound" electrons in $n-\pi^*$ transitions will require higher energy and thus should give rise to a blue shift in the absorption spectrum. If the ketones are strongly physically adsorbed, the blue shifts could well be more pronounced than typical ethanol solvent blue shifts. The highly polar nature of the adsorbant should also influence the energy requirements for $\pi-\pi^*$ transitions. In this case the excited molecules should be more strongly adsorbed than molecules in the ground state, giving rise to pronounced red shifts in the $\pi-\pi^*$ transitions, *more pronounced than in ethanol*. This is clearly what is observed. The lowest energy $\pi-\pi^*$ transition (maximum) in benzophenone in cyclohexane is at 2480 Å., in ethanol it is shifted 30 Å. to the red, and in silica gel the shift is

was poured (with agitation) into the cell. Chromatography grade activated Fisher 28-200 mesh silica gel was then slowly added to the solution in small increments by means of a tiny spatula, with considerable agitation and stirring with a fine wire. All air bubbles were removed by this technique, and the slurry took on a homogeneous appearance. The net increase in volume after addition of the silica gel was 10-15%.

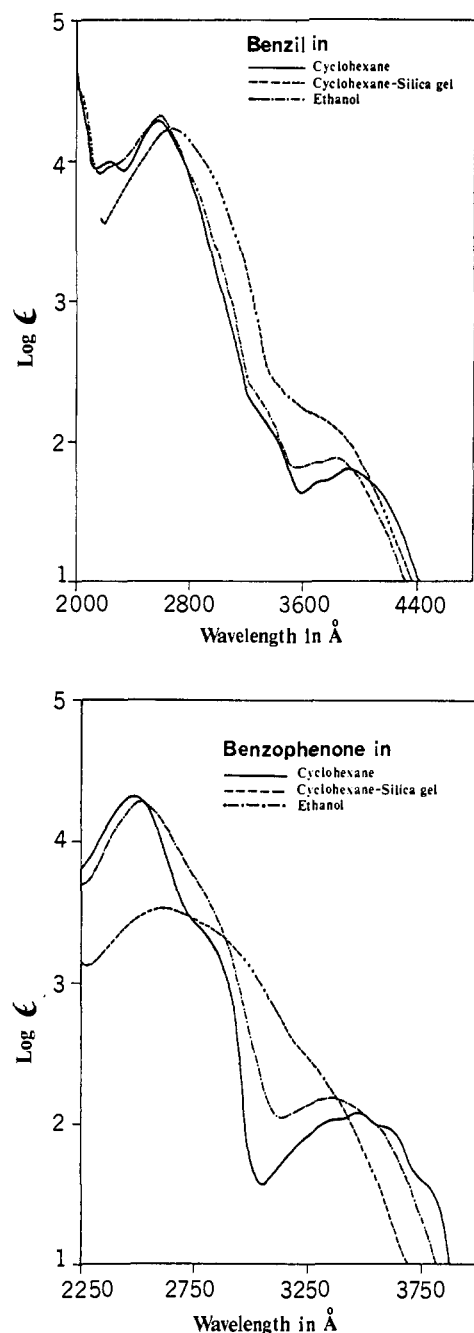


Figure 2.

135 Å. Similarly, in benzil the first $\pi-\pi^*$ band in cyclohexane is at 2570 Å. It is shifted 30 and 120 Å. in ethanol and silica gel, respectively.

The $n-\pi^*$ transitions in all of the molecules are shifted to the blue as expected. Again, the shifts are more pronounced than ethanol blue shifts. For example, the first $n-\pi^*$ transition (maximum) in tetramethyl-1,3-cyclobutanedione in cyclohexane occurs at 3510 Å. In ethanol it is shifted to the blue only 70 Å.⁶ while in the silica gel-cyclohexane matrix the blue shift is 210 Å. In the next $n-\pi^*$ transition (at 3080 Å. in cyclohexane) the ethanol blue shift is only 40 Å.⁶ while in silica gel the shift is 165 Å. Blue shifts in going from cyclohexane to the cyclohexane-silica gel matrix for the $n-\pi^*$ transitions of acetone and biacetyl

(6) E. M. Kosower, *J. Chem. Phys.*, **38**, 2813 (1963).

are, respectively, 125 and approximately 325 Å. For pyruvic acid the absorption maximum in benzene at 3525 Å. becomes a shoulder about 300 Å. toward shorter wave lengths in a silica gel slurry.

This communication has been intended only to represent a few of the possibilities that the technique offers. The photochemical behavior and emission spectra of these and related systems are currently being studied.

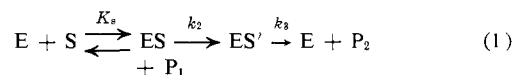
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Titration of the Active Sites of Acetylcholinesterase¹

Sir:

We wish to report the direct observation of a stoichiometric reaction in the eel acetylcholinesterase catalyzed hydrolysis of a carboxylic ester and the use of this stoichiometric reaction in the development of a procedure for the determination of the concentration (normality) of the active sites of this enzyme. *o*-Nitrophenyl dimethylcarbamate was used as the substrate. The initial rapid release of *o*-nitrophenol in this reaction is most readily interpreted in terms of the three-step kinetic scheme



where E is enzyme, S, substrate, ES, enzyme-substrate complex, ES', carbamyl-enzyme, P₁ and P₂ the alcohol and acid portions of the substrate, respectively, and k_2 and k_3 the rate constants of carbamylation and decarbamylation, respectively, the latter being rate-determining from the present results. The present direct observation of the two kinetic steps of eq. 1 corroborates earlier suggestions of this pathway² for eel acetylcholinesterase made on the basis of the reactions of phosphorus³ and carbamate^{4,5} inhibitors and non-competitive inhibition studies.⁶

The extrapolation of the concentration of *o*-nitrophenol produced by the enzyme-catalyzed hydrolysis of this substrate to zero time gives the concentration of the active sites of the enzyme, since the following conditions are shown to be satisfied: (1) $k_2 \gg k_3$; (2) $S_0 \gg K_m(\text{app})$; (3) $S \gg E$; and (4) the substrate reacts only at the active site. Points 2 and 3 may be experimentally controlled since all quantities are known, including $K_m(\text{app}) = 3 \times 10^{-6} M$.⁸ The

(1) This research was supported by grants from the National Institutes of Health.

(2) I. B. Wilson, F. Bergmann, and D. Nachmansohn, *J. Biol. Chem.*, **186**, 781 (1950).

(3) I. B. Wilson, S. Ginsburg, and C. Quan, *Arch. Biochem. Biophys.*, **77**, 286 (1958).

(4) I. B. Wilson, M. A. Hatch, and S. Ginsburg, *J. Biol. Chem.*, **235**, 2312 (1960).

(5) I. B. Wilson and M. A. Harrison, *ibid.*, **236**, 2292 (1961).

(6) I. B. Wilson and J. Alexander, *ibid.*, **237**, 1323 (1962).

(7) L. Ouellet and J. A. Stewart, *Can. J. Chem.*, **37**, 737 (1959).

(8) J. K. Stoops, unpublished results.