

Figure 1. Boron-11 nmr spectrum of KB_4H_9 in $(\text{C}_2\text{H}_5)_2\text{O}$ at -45° (32.1 MHz).

ppm to B_2 and B_4 , and the resonance at 0.4 ppm to B_3 . At lower temperatures, the two resonances at low field are broader; the triplet is essentially unchanged.

On warming the nmr sample from -45 to 0° , the triplet first loses resolution, then broadens, and disappears as the peak at 0.4 ppm also broadens and disappears and the peak at 9.7 ppm becomes sharper. At 0° , a very broad new peak is visible, and as the temperature is raised this peak becomes more intense and progressively sharper until at room temperature (see Figure 2), it has become a doublet (δ 26.5 ppm, $J = 105$ Hz). The ratio of the areas of the two resonances at room temperature is 1.0:1.0. The doublet can be attributed to B_1 and B_3 which have become equivalent on the nmr time scale due to a rapid tautomerism. The chemical shift of this doublet is equal to the arithmetic mean of separate resonances observed at low temperature and recooling the sample regenerates the original low temperature spectrum.

The competing reactions described here involving NH_3 and B_4H_{10} (deprotonation and unsymmetrical cleavage) appear to occur in the reaction of NH_3 with B_5H_{10} .^{3,15} A recent report has been made of the reaction of pentaborane(11) with ammonia to give a diammoniate salt,¹⁶ $\text{BH}_2(\text{NH}_3)_2^+\text{B}_4\text{H}_9^-$. It is of interest to note that we have evidence for the deprotonation of B_5H_{11} by NH_3 . Ammonia was frozen at -196° above a dimethyl ether solution of B_5H_{11} in an nmr tube (mole ratio 2:1). The sample was warmed to -100° in the nmr machine and the spectrum was recorded at intervals as the temperature was slowly raised to -80° . At this point the spectrum of B_5H_{11} had completely disappeared but the high-field triplet characteristic of B_4H_9^- was not present. The spectrum was very similar to that of KB_5H_{10} prepared from KH and B_5H_{11} . Furthermore, in a reaction analogous to (3) described above, NH_4I was produced and identified by X-ray powder diffraction.

(15) A preliminary report on the unsymmetrical cleavage of B_5H_{10} was presented by G. Kodama at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract INOR 10.

(16) G. Kodama, J. E. Dunning, and R. W. Parry, Abstracts, 25th Annual Northwest Regional Meeting of the American Chemical Society, June 17-18, 1970, Seattle, Wash., paper no. 98; G. Kodama, J. E. Dunning, and R. W. Parry, *J. Amer. Chem. Soc.*, submitted for publication.

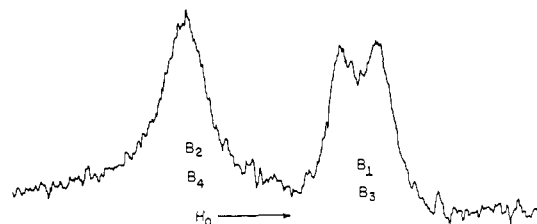
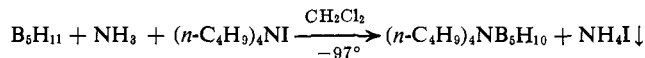


Figure 2. Boron-11 nmr spectrum of KB_4H_9 in $(\text{C}_2\text{H}_5)_2\text{O}$ at ambient temperature (32.1 MHz).

The following reaction is proposed.



It is possible that deprotonation of the boron hydrides by ammonia is a general reaction. We are continuing to explore this possibility.

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Reactive Species Mutually Isolated on Insoluble Polymeric Carriers. I. The Directed Monoacylation of Esters

Sir:

When molecules of a substance, A, are bound to an insoluble, cross-linked polymer, their free motion will be restricted due to the relative rigidity of the polymeric lattice. If the molecules are bound at the appropriate mutual distances, a situation approaching infinite dilution can thus be obtained, while actual "concentration" may still be relatively high. In this manner intermolecular reactions between the molecules of A (or reactive intermediates derived therefrom) are minimized, and, depending on the case, these molecules can be made to react either with a soluble reagent, B, or intramolecularly to give cyclic compounds.

This concept of "immobilization-on-polymer" has recently been used in the synthesis of cyclic peptides.¹⁻⁴ In this communication we wish to illustrate the general applicability of this novel approach by reporting on the directed monoacylation of polymer-bound ester enolates.

When attempting to acylate esters having more than one α -hydrogen by treating the corresponding enolate with an acyl halide, two competing reactions are reported to occur: self-condensation of the ester to be acylated and diacylation due to proton transfer from the monoacylated ester to still unreacted enolate.^{5,6}

(1) M. Fridkin, A. Patchornik, and E. Katchalski, *J. Amer. Chem. Soc.*, **87**, 4646 (1965).

(2) E. Bondi, M. Fridkin, and A. Patchornik, *Israel J. Chem.*, **6**, 22p (1968).

(3) L. Yu. Sklyarov and I. V. Shashkova, *Zh. Obshch. Khim.*, **39**, 2778 (1969).

(4) F. Flanigan and G. R. Marshall, *Tetrahedron Lett.*, 2403 (1970).

(5) B. E. Hudson, Jr., and C. R. Hauser, *J. Amer. Chem. Soc.*, **63**, 3156 (1941).

indications of the formation of 9- and 15-membered rings, respectively.

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Geometry of the Pyridine-Iodine Complex from the Effect of an External Electronic Field on Absorption

Sir:

Molecular geometries of several donor-acceptor complexes have been determined in crystals by many investigators following the initial work of Hassel and collaborators.^{1,2} Since the enthalpies of formation of these complexes are small, there have been doubts in many peoples' minds whether forces other than those present in solution or vapor contribute to the observed conformations in crystals.³ If that were the case, the molecular geometry observed in crystals could be markedly different from that in solution or vapor. At present there are no available methods for the direct determination of molecular conformation of donor-acceptor complexes in solution or vapor. This is a great disadvantage, because the charge-transfer interactions are best studied in solution or vapor and not in crystals. The purpose of this communication is to suggest that studies of the effects of the external electric fields could provide a direct method of determining the geometry of donor-acceptor complexes in solution and to report the application of this method to the pyridine-iodine complex.

Figure 1 shows two of the many possible structures for the pyridine-iodine complex. It is suggested by analogy to the crystal structure of pyridine-iodine monochloride complex.¹ II is the structure proposed by Reid and Mulliken on theoretical grounds.⁴ It should be pointed out that I or some modification of it is favored by indirect evidence. Mulliken⁵ has recently shown that the shape of the charge-transfer absorption of the pyridine-iodine complex gives strong support for I. This system is considered here mainly to illustrate the power of electric dichroism studies in structure determination. Figure 1 also gives the expected directions of dipole moment and transition moments for the 4200-Å band and the charge-transfer absorption of the complex. The 4200-Å band of the complex is assigned as a transition mainly localized on iodine⁶ and its moment is expected to be along the iodine-iodine bond. It can be seen from Figure 1 that the dipole moment and the 4200-Å absorption are oriented along the same molecular axis for structure I. Therefore, if I were the correct structure, the component of absorption polarized parallel to the external field should be larger than the one perpendicular to the external

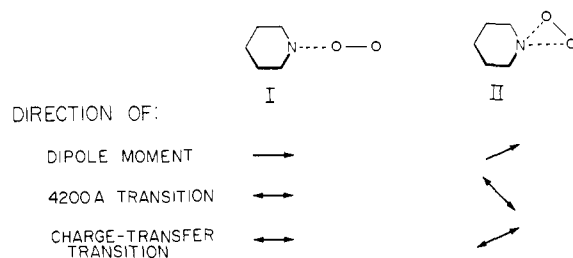


Figure 1. Two possible molecular conformations for the pyridine-iodine complex and the orientation of some moments for each conformation. These two cases are chosen for the sake of illustration only, and other possible conformations are not excluded in the interpretation of the results.

field. Exactly opposite results should be found if II were the correct structure. Thus, in the case of the pyridine-iodine complex, a qualitative study of the effects of electric fields on 4200-Å absorption should lead to the correct choice between structures I and II. If the geometry were to be intermediate between these two cases, a quantitative study should lead to its determination. In general, by a quantitative study of field effects on a sufficient number of local and charge-transfer transitions in a complex, it should be possible to uniquely determine the structure of donor-acceptor complexes.

We have determined the changes in absorption in the 4200-Å band of the pyridine-iodine complex due to an external electric field with the aid of the phase-sensitive technique.⁷ A half-wave rectified electric field of approximately 570 Hz was obtained from a high-voltage silicon rectifier (Varo VF25-15) and the secondary of a 12-kV transformer, the primary of which was connected to a power amplifier and audiooscillator. The cell consisted of two stainless-steel plates (48 mm in length and 25 mm high) suspended in a solution of 50-mm optical path. The separation between the electrodes was 1.5 mm. The change in the photocurrent induced by the electric field (for the electric vector of the light parallel and perpendicular to the field) was determined by an EMI 9558 photomultiplier tube and a Princeton Applied Research HR-8 lock-in amplifier.

Figure 2 shows the change in the photocurrent caused by the external electric field for one of the solutions investigated. Liptay^{8,9} has given a fairly complete theory of all the effects of external electric fields on dipolar molecules in solution. These effects can be classified as (i) wavelength-dependent effects which are mainly related to the change in dipole moment upon excitation and (ii) wavelength-independent effects which are related to (a) orientation of molecules by virtue of their ground-state dipole moment and (b) electrochromism (or change of the transition probability in the external electric field). At the maximum of absorption only (ii) contributes to the observed changes. Figure 2 shows that the change at the maximum is such that the absorption parallel to the field is greater

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(2) See R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, Chapter 8, for a comprehensive citation.

(3) For example, see p 216, ref 2.

(4) C. Reid and R. S. Mulliken, *J. Amer. Chem. Soc.*, **76**, 3869 (1954).

(5) R. S. Mulliken, *ibid.*, **91**, 1237 (1969); also see R. S. Mulliken and W. B. Person, *ibid.*, **91**, 3409 (1969).

(6) R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956).

(7) The experimental arrangement is similar to the one described by H. Labbert, *Tetrahedron, Suppl.*, **No. 2**, 223 (1963), and W. Liptay, W. Eberlein, H. Weidenberg, and O. Elflein, *Ber. Bunsenges. Phys. Chem.*, **71**, 548 (1967).

(8) W. Liptay, *Z. Naturforsch. A*, **21**, 1605 (1966).

(9) W. Liptay in "Modern Quantum Chemistry Part III: Action Light and Organic Crystals," O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, pp 45-66.