

Figure 1. Boron-11 nmr spectrum of KB_4H_9 in $(C_2H_5)_2O$ 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 NH₃ with B_6H_{10} .^{5,15} A recent report has been made of the reaction of pentaborane(11) with ammonia to give a diammoniate salt,¹⁶ BH₂(NH₃)₂+B₄H₉-. It is of interest to note that we have evidence for the deprotonation of B_5H_{11} by NH₃. 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 KB5H10 prepared from KH and B_5H_{11} . Furthermore, in a reaction analogous to (3) described above, NH₄I was produced and identified by X-ray powder diffraction.



Figure 2. Boron-11 nmr spectrum of KB_4H_9 in $(C_2H_5)_2O$ at ambient temperature (32.1 MHz).

The following reaction is proposed.

$$B_{5}H_{11} + NH_{3} + (n - C_{4}H_{9})_{4}NI \xrightarrow[-97^{\circ}]{-97^{\circ}} (n - C_{4}H_{9})_{4}NB_{5}H_{10} + NH_{4}I \downarrow$$

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

Acknowledgment. We wish to acknowledge, gratefully, support of this research by the National Science Foundation.

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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}

⁽¹⁵⁾ A preliminary report on the unsymmetrical cleavage of $B_{e}H_{10}$ 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.

⁽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 (1999),

⁽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).

Ester	Acylating agent	Product	Mp, °C (lit.)	Yield,ª	Yield of unreacted acid, %
●-CH ₂ OCOCH ₂ C ₆ H ₅	p-NO ₂ C ₆ H ₄ COCl	$p-NO_2C_6H_4COCH_2C_6H_5$ 7	159–160 (160–160, 5) ^b	43	40
\bigcirc -CH ₂ OCOCH ₂ C ₆ H ₅	<i>p</i> -BrC ₆ H ₄ COCl	$p-BrC_6H_4COCH_2C_6H_5$ 8	104–105 (103)°	40	45
\bigcirc -CH ₂ OCOCH ₂ C ₆ H ₅	$(\alpha$ -C ₁₀ H ₇ CH ₂ CO) ₂ O	α -C ₁₀ H ₇ CH ₂ COCH ₂ C ₆ H ₅ 9	57-58 (58, 5-59) ^d	40	55°
P-CH ₂ OCOCH ₃	<i>p</i> -NO₂C ₆ H₄COCl	$p-NO_2C_6H_4COCH_3$ 10	80-81 (78.5-80)/	20	45

^a Based on the amount of purified product relative to that of starting ester. ^b H. Zimmer and J. P. Bercz, Justus Liebigs Ann. Chem., 686, 107 (1965). ^c G. I. Chervenyuk and V. P. Kravets, Ukr. Khim. Zh., 30, 1335 (1964); Chem. Abstr., 62, 9051e (1965). ^d Ch. Ivanov and L. Mladenova-Orlinova, Angew. Chem., 76, 301(1964). ^e In this case polystyrene-25% divinylbenzene was used as the carrier. ^f H. G. Walker and C. R. Hauser, J. Amer. Chem. Soc., 68, 1386 (1946).

In the following it is shown that these side reactions can be avoided by "immobilizing" the ester enolates to be acylated on insoluble polymeric carriers, thus separating them from each other and from un-ionized ester molecules.

Polymer esters of phenylacetic and acetic acids (3; 0.1-0.3 mmol of ester/g of polymer⁷) were prepared by reaction of either acid (2) with chloromethylated polystyrene-2% divinylbenzene (1).⁹ The remaining chloromethyl groups were treated with excess ethyl mercaptan.

The polymer ester was swelled in toluene–20% 1,2dimethoxyethane and then converted into the enolate by the action of an equivalent amount of trityllithium in tetrahydrofuran¹⁰ at 0° under dry argon.

$$\begin{array}{c} \textcircled{P}-CH_{2}Cl + R_{1}CH_{2}CO_{2}H \longrightarrow \textcircled{P}-CH_{2}OCOCH_{2}R_{1} \xrightarrow{(Ph)_{3}CLi} \\ 1 & 2 & 3 \end{array} \\ \begin{array}{c} \textcircled{P}-CH_{2}OCOCHR_{1} \xrightarrow{R_{2}COX} \textcircled{P}-CH_{2}OCOCH(R_{1})COR_{2} \xrightarrow{HB_{1}-CF_{3}CO_{2}H} \\ 4 & 5 & R_{2}COCH_{2}R \end{array} \\ \begin{array}{c} \textcircled{P}= insoluble polymer \\ X = Cl or OCOR_{2} \end{array}$$

After the disappearance of the red color of the base (1-5 min), 1.5 equiv of an acid chloride or anhydride was added and the mixture stirred for 1 hr at room temperature. The polymer was then filtered, washed thoroughly with benzene, water, and methanol, and dried. Upon cleavage with dry HBr in trifluoroacetic acid at room temperature a single ketone 6 and unreacted acid were obtained in every case [thin layer chromatography (tlc)]. The ketones were identified by their melting points and by nmr, ir, and mass spectra. Results are summarized in Table I.

In an analogous reaction in solution, performed under identical conditions, several ketonic products were formed. Ethyl phenylacetate was added to a trityllithium solution until the red color disappeared (final

berger's method⁸ as modified in our laboratory by S. Rogozinski. (8) G. Ingram in "Comprehensive Analytical Chemistry," Vol. IB, C. L. Wilson and D. W. Wilson, Ed., Elsevier, Amsterdam, 1960, p 642.

(9) R. B. Merrifield, J. Amer. Chem. Soc., 85, 2149 (1963).
(10) P. Tomboulian and K. Stehower, J. Org. Chem., 33, 1509 (1968).

concentration of the ester was 0.2 *M*). Treatment with *p*-nitrobenzoyl chloride (as described above) and workup yielded a mixture containing five 2,4-dinitrophenylhydrazine (DNP)-positive compounds (tlc). After hydrolysis with H_2SO_4 -HOAc- H_2O still five DNPpositive compounds were detected.¹¹ The yield of 4'-nitro-2-phenylacetophenone (7) was 22%.

In order for the "immobilization" method to succeed, concentrations of the species bound to the polymer must not be too high. Thus when polymer phenylacetate, 1.5 mmol/g, was treated with sodium *tert*-amylate for 45 min at 80°, a product of ester condensation, dibenzyl ketone, was obtained upon cleavage (mp 35°; 4% yield). Also, when polymer acetate, 2 mmol/g, was treated with *p*-nitrobenzoyl chloride (trityllithium as base, room temperature) two ketones were obtained upon cleavage: the desired 4'-nitroacetophenone (10, 4% yield) and *p*-nitrobenzoylacetone (10\%, mp 110°, lit.¹² 111–113°; molecular peak *m/e* 207). The latter is apparently formed by nitrobenzoylation of the ester condensation product, \bigcirc –OCOCH₂COCH₃.

Spectroscopic evidence for a polymeric dilution effect was observed in the ir spectra of compounds of the type $\bigcirc -O(CH_2)_nOH$. These alcohols were obtained by treating chloromethylated polystyrene-2% divinylbenzene with an excess of the monosodium salts of α, ω -diols. The compound derived from ethylene glycol, $\bigcirc -OCH_2CH_2OH$ (1 mmol/g), showed mainly a free OH absorption (3580 cm⁻¹, sharp; KBr), while the corresponding 1,4-butanediol derivative, $\bigcirc -O(CH_2)_4OH$ (1 mmol/g), showed both a weak free OH band and a much stronger hydrogen-bonded OH absorption (3300 cm⁻¹ broad).¹³

At present we are studying other directed carbanionic reactions of polymer-bound species, including various cyclization reactions. In preliminary experiments, we have obtained by this method good yields of pure carbocyclic compounds having simple (five- and sixmembered) rings. We used the reaction of α, ω dibromoalkanes with polymer-bound malonate, $\bigcirc -\text{OCOCH}_2\text{COOC}_2\text{H}_3$, and the Dieckmann cyclization of diesters of the type $\bigcirc -\text{OCO}(\text{CH}_2)_n\text{COOR}$. When *n* was 8 and 14 in the Dieckmann cyclization, there were

⁽⁶⁾ D. F. Thomson, P. L. Bayless, and C. R. Hauser, J. Org. Chem., 19, 1490 (1954).

⁽⁷⁾ Determined in the case of phenylacetic acid by gas chromatography of methyl phenylacetate, obtained by hydrolysis of polymer phenylacetate and esterification of the released acid. In the case of acetic acid esters, acetyl residues on the polymer were determined by Wiesenberger's method⁸ as modified in our laboratory by **S.** Rogozinski.

⁽¹¹⁾ No attempt was made to identify all ketones either before or after hydrolysis.

⁽¹²⁾ A. Sieglitz and O. Horn, Chem. Ber., 84, 607 (1951).

⁽¹³⁾ L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958, pp 96-99.

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.⁸ 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 donoracceptor 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 pyridineiodine 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 iodineiodine 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

- (1) O. Hasse and C. Rohming, Acta Chem. Scana., 10, 050 (1950).
 (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).





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 chargetransfer 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 phasesensitive 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

⁽¹⁾ O. Hassel and C. Romming, Acta Chem. Scand., 10, 696 (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.