

## Studies of the Solid-State Rearrangement of $\alpha$ -Phenylazo- $\beta$ -benzoyloxystilbene

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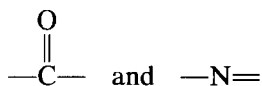
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### Introduction

Solid-state organic chemistry is being more widely recognized as a fertile area for studying the effects of geometry on reaction rates and mechanisms (1-8). A reaction which offers an opportunity for a comparison study in solution and in the solid state, because it yields the same products in both, is described. While the products which are formed are the same, the factors which determine the rate and perhaps mechanism are chemical in solution and probably physical in the solid state. This study is being done in order to investigate how physical properties in the solid can affect the mechanism of the reaction.

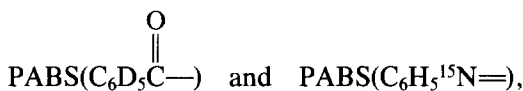
$\alpha$  - Phenylazo -  $\beta$  - benzoyloxystilbene (PABS, 1) rearranges in quantitative yield to benzil benzoylphenylhydrazone (BBPH, 2) in solution and in the solid state (9). Kinetic studies in decalin solution have shown that the reaction is first order and is remarkably insensitive to substituents in the migrating group. It was proposed that the starting material is a trans stilbene and that the rate-determining step of the rearrangement is isomerization to the cis isomer, bringing



closer together. The isomerization is followed by a rapid intramolecular rearrangement to BBPH (10). The rearrangement might occur during the isomerization and before the cis isomer actually forms. This suggestion has been corroborated in large part by Pendergrass *et al.* (11), who have studied the analogous rearrangement of 3(a, b) to 4(a, b). They showed crystallographically that 3(b) has the trans configuration at the C=C and N=N double bonds.

This work attempts to extract a rate law for the solid-state reaction anticipating that physical factors may control the rate (12). It is noteworthy in this regard that the reaction rate is fastest for the melt and slowest in the solid. Also, the product forms sublimable needles which coat the surface of the crystal of the starting material (10).

This work also attempts to determine whether the rearrangement is intra- or intermolecular in solution, in the melt, and in the solid. It has been accomplished by means of a cross-over experiment with PABS labelled with deuterium in the benzoyl group and  $^{15}\text{N}$  in the phenylazo group designated



respectively. The isotope compositions of

starting materials and products have been confirmed by mass spectrometry.

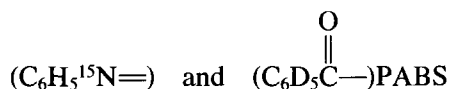
### Materials and Methods

(C<sub>6</sub>D<sub>5</sub>)Benzoyl chloride (99 atom% D) was obtained from MSD Isotopes (Montreal, Canada). [<sup>15</sup>N]Aniline (95% <sup>15</sup>N) was purchased from Junta de Energia Nuclear (Madrid, Spain). All other chemicals were reagent grade or better. Spectra were measured in a Cary 15 spectrophotometer. Mass spectra were obtained in the Ribermag R-10-10 mass spectrometer at the Department of Chemistry, Columbia University, New York.

[<sup>15</sup>N]Phenylhydrazine was prepared by Donald McCain (City College undergraduate research, MBRS) from [<sup>15</sup>N]aniline, sodium nitrite, and sodium sulfite. [<sup>15</sup>N]Benzilphenylhydrazone (BPH) was prepared from equimolar quantities (1.4 mmole) of [<sup>15</sup>N]phenylhydrazine and benzil in 2.5 ml ethanol and a drop of conc. HCl. After warming on a steam bath, the mixture was cooled and refrigerated to complete crystallization. After filtration and washing with ethanol, (C<sub>6</sub>H<sub>5</sub><sup>15</sup>NH—)BPH (82% yield) was obtained.

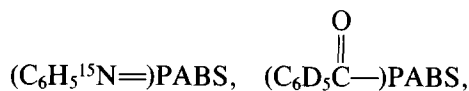
(C<sub>6</sub>H<sub>5</sub><sup>15</sup>N=)PABS and (C<sub>6</sub>D<sub>5</sub>C=)PABS were prepared as previously described (9), the former from (C<sub>6</sub>H<sub>5</sub><sup>15</sup>NH—)BPH and benzoyl chloride and the latter from BPH and (C<sub>6</sub>D<sub>5</sub>)benzoyl chloride.

Mixtures of



were dissolved in benzene and crystallized from benzene/hexane and rearranged in decalin solution, in the melt, and in the solid state at 95°C on a hot stage. No melting was observed during the course of the solid-state rearrangement.

The mass spectra of



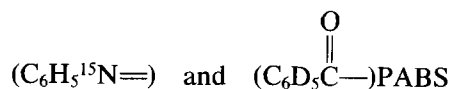
the mixture, and the rearrangement products obtained under different conditions (melt, solid, solution) were determined using chemical ionization (CH<sub>4</sub>) and field desorption.

For kinetic studies, 10 mg of PABS was placed in a long (10 ml), sealed Pyrex tube and immersed for almost the whole length of the tube in a Lauda Constant Temperature Bath at 100.1°–100.2°C. No melting was observed during the course of the reaction. Aliquots of about 1 mg were removed daily, weighed on a Cahn Microbalance (Model 26), and dissolved in 100 ml isoctane (MCB Spectrograde). The percentages of PABS and BBPH in the mixture were determined spectroscopically as previously described (10). The reaction was followed to at least 50% completion. The results were the same for crystals and crushed crystals, for atmospheric and reduced (0.5–0.6 mm) pressure.

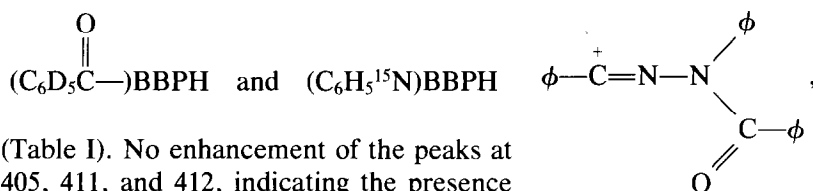
### Results and Discussion

This reaction is a good model system, giving one product in quantitative yield in solution, melt, and solid. Enough is known about the reaction in solution and about the structure of the starting material, including the atomic coordinates in the crystal lattice for one crystalline form, to probe for the events and conditions which promote reaction in the solid.

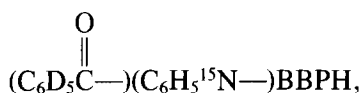
The mass spectra of mixtures of



which had been quantitatively rearranged in solution, in the solid state, or in the melt corresponded to



(Table I). No enhancement of the peaks at 405, 411, and 412, indicating the presence of the cross-reacted products, BBPH, or

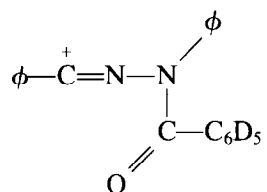
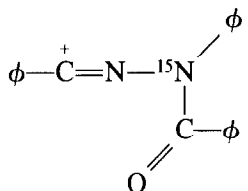


respectively, was observed.

The fragmentation patterns confirm these observations. For unlabelled PABS and BBPH, a M-105 ( $\phi-\text{C}=\text{O}$ ) peak at 299 was observed. For  $(\text{C}_6\text{H}_5^{15}\text{N}=\text{O})[\text{PABS or BBPH}]$  this peak was at 300 and for



it was at 304. These results indicate three things. The fragments must be



respectively. There is no evidence for a doubly labelled fragment. This type of fragment can only come from BBPH; therefore there is rearrangement of PABS in the spectrometer to BBPH. This arrangement, as

TABLE I  
MASS SPECTRA (CI, CH<sub>4</sub>) FOR PABS AND BBPH WITH AND WITHOUT ISOTOPES BEFORE AND AFTER  
REARRANGEMENT: RELATIVE INTENSITIES FOR PERTINENT PEAKS

M/e + 1	BBPH	PABS	(C <sub>6</sub> D <sub>5</sub> )PABS	[ <sup>15</sup> N]PABS	[ <sup>15</sup> N](+C <sub>6</sub> D <sub>5</sub> )PABS	Rearranged mixture		
						Solid	Melt	Solution
299	82	55						
300	22	14		32	27	79	74	
301	7	3		9	8	20	22	
302				3	3	3	8	
304			73		19	59	53	
305			20		6	16	14	
306			3		1	2	2	
405	100	100						
406	31	34		100	100	100	100	100
407	5	5		33	34	31	31	32
408				6	6	5	5	4
410			100		75	73	76	76
411			35		27	26	24	27
412			6		5	5	4	5
Ratio 406/410					1.4	1.3	1.4	1.3

TABLE II

A. Change of $\alpha$ as a function of time for a typical kinetic run at 100°C			
Time elapsed in hr (days)	$\alpha$		
22 (0.92)	0.10		
67 (2.8)	0.26		
166 (6.9)	0.36		
237 (9.9)	0.45		
379 (15)	0.57		

B. Plots of $t$ versus various functions of $\alpha$			
Function of	Slope	Intercept	Correlation
$\alpha^2$	0.000807	0.004	0.992
$(1 - \alpha)\ln(1 - \alpha) + \alpha$	0.00051	-0.0015	0.990
$[1 - (1 - \alpha)^{1/3}]^2$	0.0015	-0.0017	0.985
$1 - \alpha$	-0.0014	0.885	0.896
$1 - (1 - \alpha)^{1/2}$	0.00938	0.035	0.953
$1 - (1 - \alpha)^{1/3}$	0.000649	0.023	0.956
$\ln \alpha$	0.00626	-2.14	0.850
$[-\ln(1 - \alpha)]^{1/4}$	0.00257	0.376	0.749
$[-\ln(1 - \alpha)]^{1/3}$	0.00260	0.315	0.800
$[-\ln(1 - \alpha)]^{1/2}$	0.00257	0.220	0.873
$[-\ln(1 - \alpha)]^{2/3}$	0.00247	0.151	0.917

well as the melt, solution, and solid-state rearrangements, is intramolecular.

In the kinetic studies of the solid-state rearrangement, the fraction ( $\alpha$ ) of PABS converted as a function of time ( $t$ ) was determined (Table IIA).

The methods of Brindley *et al.* (13), Han-

cock and Sharp (14), and O'Brien (15) were used to fit the results to a rate law. Several runs with crystals and crushed crystals at atmospheric pressure and at 0.5–0.6 mm gave the same results. The reaction fits the diffusion-controlled rate law the best (Table IIB). This is consistent with microscopic observation of the reaction. Plots of time ( $t$ ) against  $\alpha^2$  or  $(1 - \alpha)\ln(1 - \alpha) + \alpha$  are linear with a correlation coefficient of 0.99 (15) and a plot of  $\ln[-\ln(1 - \alpha)]$  versus  $\ln t$  has a slope of 0.62 (14, 16). Indeed, observations of the rearrangement of a red nugget of PABS on the hot stage of a microscope at 105°C show the appearance of "whiskers" of pale yellow BBPH on the surface while the overall shape of the nugget remains the same. The product may be subliming up to the surface from "holes" or forming on the surface. However, running the reaction at reduced pressure did not increase the rate.

The structure of 1(d) was determined by X-ray diffraction by Bray *et al.* (12) (Fig. 1). The C=C and N=N double bonds have trans configurations. There is a slight deviation from planarity in the region of the C=C double bond.

There appear to be no significantly short intermolecular contacts which might favor

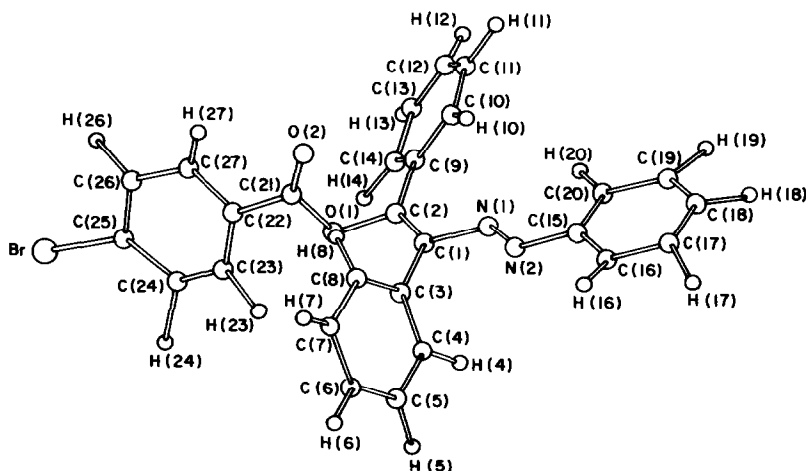


FIG. 1. Structure of  $\text{BrC}_{17}\text{H}_{19}\text{N}_2\text{O}_2$ .

intermolecular rearrangement. The distance between the rearrangement termini explains the low rate of thermal rearrangement in the solid as compared to that in the melt and in solution. In the melt at 150°C the rearrangement is complete in minutes, in decalin solution at 102°C the reaction is 90% complete in 6 hr, and in the solid at 100°C only 10% rearrangement has occurred after 22 hr. The reaction in solution is unimolecular and therefore undoubtedly intramolecular, but the molecular packing does not suggest a mechanism for the intramolecular solid-state reaction. Rotation or twist around the  $C_1=C_2$  bond as well as rotation around the  $C_1-N_1$ ,  $C_2-O_1$ , and  $C_{21}-O_1$  single bonds must occur in order for the rearrangement termini  $N_2$  and  $C_{21}$  to come within bonding distance to form the amide bond.

The cis configuration around  $C_1=C_2$  would be too crowded and rearrangement during the incipient isomerization would relieve the crowding. The cis isomer probably does not form or is extremely short-lived. An alternative mechanism is a transitory break of the  $C_{21}-O_1$  bond and sliding of  $\phi-C=O$  along the  $\pi$  system  $C_2=C_1-N_1=N_2$  to  $N_2$ . This kind of molecular motion would be most apt to occur on the surface of the crystal or at dislocation sites and planar faults where local conditions would have some of the features of the melt. The product, which can sublime from the reaction site, would increase the number and size of holes and disrupt the crystal packing further.

It is predicted that the rearrangement product, BBPH, will be exclusively one isomer, the cis isomer (2). Unlike the analogous benzoylphenylhydrazone (IV), two possible geometric isomers are possible. The intramolecular nature of the rearrange-

ment will dictate only one geometric isomer at  $C=N$ . The X-ray structure of the solid-state rearranged BBPH is being elucidated. The nature of the stereochemistry around the  $C=N$  may provide an insight into the dynamics of the rearrangement.

### Acknowledgment

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