

**Table III**  
Equilibrium Constants for Variable-Temperature  
Dissociation of Ureas

| Urea 6   |      | Urea 4   |      | Urea 3   |                       |
|----------|------|----------|------|----------|-----------------------|
| Temp, °C | K    | Temp, °C | K    | Temp, °C | K                     |
| 32       | 0.70 | 44.5     | 0.31 | 103      | $8.3 \times 10^{-3}$  |
| 34.5     | 0.89 | 48.5     | 0.40 | 109      | $1.25 \times 10^{-2}$ |
| 39       | 1.10 | 52.5     | 0.55 | 120.5    | $2.8 \times 10^{-2}$  |
| 50       | 2.4  | 61       | 0.94 | 127      | $4.1 \times 10^{-2}$  |
| 55       | 2.6  | 65       | 1.57 | 134      | $7.0 \times 10^{-2}$  |
| 59       | 4.0  | 69       | 2.1  | 138      | $1.0 \times 10^{-1}$  |
| 65.5     | 5.5  | 73.5     | 2.7  | 143      | $1.3 \times 10^{-1}$  |
|          |      | 81.5     | 4.5  |          |                       |

**Table IV**  
Chemical Shift Values<sup>a</sup> of the Benzylic Methyl Groups  
in Each Urea and the Isocyanate at 34°

| Compd | $\delta$ | Compd | $\delta$ |
|-------|----------|-------|----------|
| 1     | 1.29     | 6     | 1.23     |
| 2     | 1.27     | 7     | 1.24     |
| 3     | 1.26     | 8     | 1.22     |
| 4     | 1.26     | 9     | 1.36     |
| 5     | 1.26     |       |          |

<sup>a</sup> In parts per million upfield from anisole OCH<sub>3</sub>.

groups of the isocyanate and the urea were recorded at 100-Hz sweep width and measured with a planimeter. In the case of this particular urea, the concentration of the amine could be measured as well. The *tert*-butyl groups and the methyls of the isopropyl groups were at  $\delta$  2.44 and 2.51. The corresponding peaks in the urea were at  $\delta$  2.12 and 2.25 ppm upfield from anisole OCH<sub>3</sub>.

The equilibrium constants (Table I) were calculated using a correction for the density of anisole at each temperature.<sup>15</sup> The thermodynamic values (Table II) were obtained by a least-squares treatment of  $\log K$  vs.  $1/T$ . The temperatures could be measured quickly after each equilibration if a very fine sealed capillary of ethylene glycol was placed in the nmr tube with the sample. The ethylene glycol peaks occur in an otherwise clear area of the spectrum.

Urea 6 was prepared similarly, although the pentane solution required cooling for crystallization of the product.

Urea 3 gave no precipitate; so it was prepared by transferring the amine, isocyanate, and anisole with syringes in a glove bag under nitrogen to the nmr tube, weighing after each addition.

Equilibrium constants (Table III) were determined from solutions of each of the above ureas at two different concentrations to check reproducibility.

Ureas 1, 2, 5, 7, and 8 were measured at only one temperature owing to very slow equilibration, or their dissociating near the upper limit of the usable temperature range. They were each prepared in the nmr tubes as described above for 3. See Table IV for chemical shift values.

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**Registry No.**—1, 51608-96-9; 2, 51608-97-0; 3, 51608-98-1; 4, 51608-99-2; 5, 51609-00-8; 6, 51609-01-9; 7, 51609-02-0; 8, 51609-03-1; 9, 28556-81-2; di-*sec*-butylamine, 626-23-3; cyclohexyl-3-pentylamine, 51609-04-2; dicyclohexylamine, 101-83-7; *tert*-butylisopropylamine, 7515-80-2; *tert*-butyl-3-pentylamine, 51609-05-3; *tert*-butylcyclohexylamine, 51609-06-4; isopropyl(2,4,4-trimethyl-2-pentyl)amine, 51609-07-5; 2,2,6,6-tetramethylpiperidine, 768-66-1; cyclohexylamine, 108-91-8; 2-butanone, 78-93-3; 2,6-dimethylaniline hydrochloride, 21436-98-6.

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### Heterodienophiles. VI.<sup>1</sup> The Structure of Protonated Aldimines

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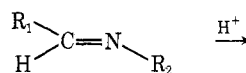
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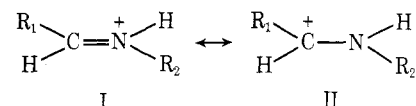
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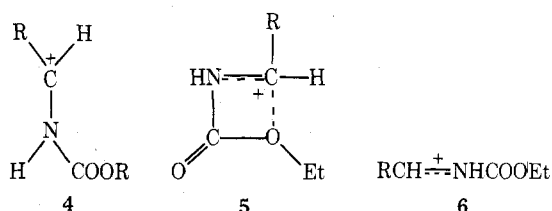
A nuclear magnetic resonance study<sup>2</sup> of protonated aldimines 1-3 with fluorosulfonic acid-antimony pentafluoride in sulfur dioxide solution has indicated a predominance of *E*-immonium structure I, with only limited contribution of aminocarbonium ion form II. We have extended this study in strongly acidic solution to aldimines having electron-withdrawing *N*-carbonyl, acyl, and *p*-toluene-sulfonyl substituents.



- $R_1 = \text{Ph}; R_2 = \text{CH}_3$
- $R_1 = \text{Ph}; R_2 = \text{Ph}$
- $R_1 = \text{Ph}; R_2 = \text{Ph-}p\text{-Cl}$



A literature survey indicates that reactions of *N*-carbethoxyl imines have been variously described as polar cycloadditions,<sup>3</sup> Diels-Alder reactions,<sup>4</sup> pseudo-Diels-Alder reactions,<sup>5</sup>  $\alpha$ -amidoalkylations,<sup>6</sup> or stabilized carbonium ion reactions.<sup>7</sup> The reactive species in these reactions has been depicted as an azacarbonium ion<sup>3</sup> 4, an



azacarbonium ion stabilized by ester oxygen<sup>8</sup> 5, a resonance-stabilized carbonium ion<sup>7,9</sup> 6, an *N*-protonated *Z*-immonium ion<sup>5</sup> 7, and a carbonyl-oxygen protonated *E*-iminourethane 9. One might in addition postulate an *E*-immonium ion 8 similar to 7, as well as significant contri-

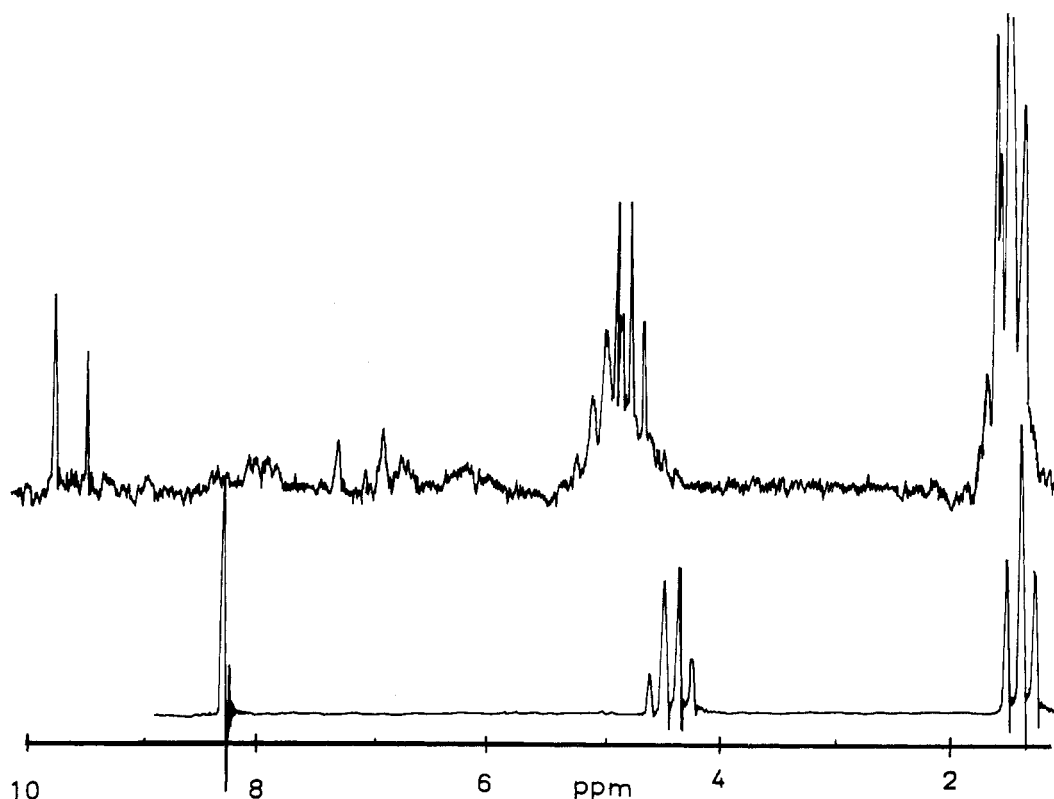
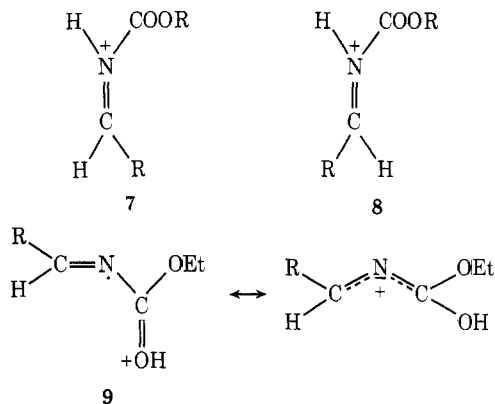


Figure 1.  $\text{CCl}_3\text{CH}=\text{NCOOEt}$  ( $\text{SO}_2$ ): lower, free imine; upper,  $\text{SbF}_5\text{-HF}_5\text{SO}_3$  added, imine doublet at  $\delta$  9.40.

tribution from a hydroxyazaallyl cation resonance contributor to 9. The various structural possibilities for protonated iminocarbamates are associated with differing steric and electronic properties. Accordingly, determination of the site of protonation is crucial if Lewis acid catalyzed heterodienophilic imine cycloadditions are to be understood and best utilized in synthesis.<sup>10</sup>



### Results and Discussion

The nmr spectral data for the methine hydrogen of trichloromethyl-*N*-carbethoxyimine<sup>11</sup> (10) in sulfur dioxide solution at  $-20^\circ$  both with and without fluorosulfonic acid-antimony pentafluoride added is shown in Figure 1 and summarized in Table I. The methine proton of 10 appears as a singlet which upon protonation of the imine is shifted downfield  $\delta$  1.10 and is split by an NH proton into a doublet,  $J = 17$  Hz.

It previously has been noted<sup>2</sup> that the magnitude of trans-coupling constants through a double bond does not change much in isoelectronic molecules; so the nmr coupling data is in best agreement with an *E*-immonium ion structure 8 for protonated imine 10, rather than with structures 4, 5, 7, or 9. Although some contribution from

structure 6 may be present, the coupling information and the small deshielding observed for the methine hydrogen indicates little charge delocalization away from nitrogen. Consistent with this interpretation, the magnitudes of both the small downfield shift of the methine resonance position upon imine protonation and of the methine to NH proton coupling are similar to those observed for *N*-alkyl and *N*-aryl immonium ion species 1-3 (Table I), for which azacarbonium ion structures have been largely precluded.<sup>2</sup>

The preferential *N*-protonation of iminocarbamate 10 can be contrasted with carbonyl-oxygen protonation of *N*-alkyl carbamates,<sup>12</sup> of  $\alpha,\beta$ -unsaturated aldehydes and ketones,<sup>13</sup> whose conjugate acids are hydroxyallyl cations in nature, and of  $\alpha,\beta$ -unsaturated acids.<sup>14</sup>

*E*-Immonium ions have also been observed (Table I) upon *N*-protonation of phenyl-*N*-*p*-toluenesulfonylimine<sup>15a</sup> (11), trichloromethyl-*N*-*p*-toluenesulfonylimine<sup>15b</sup> (12), and the immonium ions 14, formed from *N*-benzoyl- $\alpha$ -methoxybenzylamine<sup>16</sup> (13), and 17, formed from benzaldehyde bisurethane<sup>4</sup> (15). For all imines studied, the NH proton could not be observed because of broadening due to quadrupole interaction of the nitrogen and contributions of coupling to NH broadening. Failure to observe coupling is not due to rapid exchange, since splitting of the methine proton by the NH proton is observed.<sup>2</sup> Methylenebisurethane<sup>4</sup> 16 failed to eliminate urethane, *N*-hydroxymethylbenzamide<sup>17</sup> failed to dehydrate, and  $\alpha$ -methoxy-*N*-phenylhydantoin<sup>18</sup> decomposed in the strongly acidic solutions used; so protonated imines were not observed with these compounds.

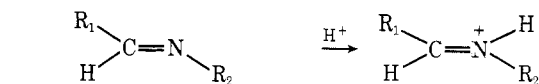
The observation of *N*-protonated immonium ions as the thermodynamically most stable isomeric species<sup>13</sup> suggests a reinterpretation of the reactivity course of Lewis acid catalyzed reactions involving alkylidenebisurethane 15.<sup>10</sup> Lewis acid decomposition of 15 results in formation of a protonated immonium ion 17. In the synthesis of bicyclic moieties<sup>10</sup> 18, using 17 and cyclo-

**Table I**  
Nmr Chemical Shifts and Coupling Constants of the Methine Hydrogen ( $H_1$ ) of Aldimines

| Structure            | $R_1$          | $R_2$                              | Solvent         | Temp, °C | Protonated <sup>a</sup> |               |                |                         |
|----------------------|----------------|------------------------------------|-----------------|----------|-------------------------|---------------|----------------|-------------------------|
|                      |                |                                    |                 |          | $H_1, \delta$           | $H_1, \delta$ | $\Delta\delta$ | $J_{H_1-NH}, \text{Hz}$ |
| <b>1<sup>b</sup></b> | Ph             | Me                                 | $\text{CDCl}_3$ | -30      | 7.99                    |               |                |                         |
|                      |                |                                    |                 | -30      |                         | 8.70          | -0.71          | 16.9                    |
| <b>2<sup>b</sup></b> | Ph             | Ph                                 | $\text{SO}_2$   | -20      | 8.17                    |               |                |                         |
|                      |                |                                    |                 | -40      |                         | 9.35          | -1.18          | 18                      |
| <b>3<sup>b</sup></b> | Ph             | Ph- <i>p</i> -Cl                   | $\text{SO}_2$   | -30      | 8.32                    |               |                |                         |
|                      |                |                                    |                 | -30      |                         | 9.27          | -0.95          | 17.2                    |
| <b>10</b>            | $\text{CCl}_3$ | $\text{CO}_2\text{Et}$             | $\text{SO}_2$   | -20      | 8.30                    |               |                |                         |
| <b>11</b>            | Ph             | $\text{SO}_2\text{Ph-}p\text{-Me}$ | $\text{SO}_2$   | -20      | 8.80                    |               |                |                         |
|                      |                |                                    |                 | -20      |                         | 9.40          | -1.10          | 17                      |
| <b>12</b>            | $\text{CCl}_3$ | $\text{SO}_2\text{Ph-}p\text{-Me}$ | $\text{SO}_2$   | -20      | 8.25                    |               |                |                         |
|                      |                |                                    |                 | -20      |                         | 9.40          | -1.15          | 17                      |
| <b>14</b>            | Ph             | $\text{COPh}$                      | $\text{SO}_2$   | -20      |                         | 9.83          |                | 17                      |
| <b>17</b>            | Ph             | $\text{CO}_2\text{Et}$             | $\text{SO}_2$   | -20      |                         | 9.05          |                | 17                      |

<sup>a</sup>  $\text{SO}_2\text{-HSO}_3\text{F-SbF}_5$ . <sup>b</sup> G. Olah and P. Kreienbühl, *J. Amer. Chem. Soc.*, **89**, 4756 (1967).

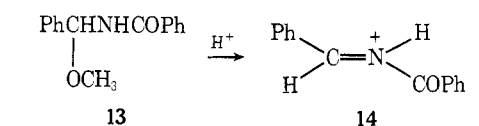
hexa-1,3-diene, *exo-R* stereoselectivity was observed to be a function of solvent and Lewis acid catalyst. Although



10,  $R_1 = \text{CCl}_3$ ;  $R_2 = \text{COOEt}$

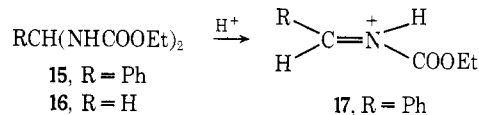
11,  $R_1 = \text{Ph}$ ;  $R_2 = \text{SO}_2\text{Ph-}p\text{-CH}_3$

12,  $R_1 = \text{CCl}_3$ ;  $R_2 = \text{SO}_2\text{Ph-}p\text{-CH}_3$



13

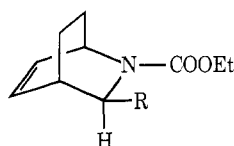
14



15,  $R = \text{Ph}$

16,  $R = \text{H}$

17,  $R = \text{Ph}$



18

stereochemical differences could be rationalized by assuming carbonyl-oxygen Lewis acid coordinated imines as reactive species, it now appears likely that N-protonated imines are formed in the decomposition of alkylidene-bisurethanes regardless of the Lewis acid employed. N-Coordination of a wide variety of sterically different Lewis acid catalysts would certainly have been expected to result in wider stereochemical variation than the 73–91% range in *exo*-phenyl selectivity observed.<sup>10</sup> Stereochemical differences are more likely the result of temperature, solvent polarity, and medium acidity effects. Preliminary studies of Lewis acid effects on the stereochemistry of cycloadditions with independently synthesized imines are in progress to confirm this suggestion.

#### Experimental Section

Trichloromethyl-*N*-carboethoxy,<sup>11</sup> trichloromethyl-*N-p*-toluenesulfonyl,<sup>16b</sup> and phenyl-*N-p*-toluenesulfonylimine<sup>15a</sup> were synthesized according to literature procedures, as were *N*-benzoyl- $\alpha$ -

methoxybenzylamine,<sup>16</sup> *N*-hydroxymethylbenzamide,<sup>17</sup> methylenebisurethane,<sup>4</sup> benzalbisurethane,<sup>4</sup> and  $\alpha$ -methoxy-*N*-phenylhydantoin.<sup>18</sup>

**Protonation of Imines.** The samples were prepared by condensing  $\text{SO}_2$  directly into an nmr tube containing the sample *via* liquid nitrogen. Acidification took place by the addition of small amounts of  $\text{FSO}_3\text{H-SbF}_5$  accompanied by vigorous stirring as the sample was warmed to  $-20^\circ$ .

**Nmr spectra.** Spectra were obtained using a Varian A-60 spectrometer equipped with V-6040 variable-temperature probe and accessories. Temperatures were measured using the methanol standard supplied by Varian. The Van Geet<sup>19</sup> correction was incorporated.

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**Registry No.**—1, 25521-74-8; 2, 1750-36-3; 3, 1613-89-4; 10, 51608-59-4; 11, 51608-60-7; 12, 51608-61-8; 14, 51608-62-9; 17, 51608-63-0.

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