

# The Chemistry of Aminimides

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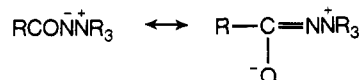
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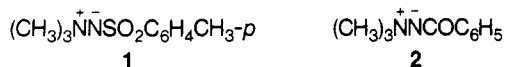
nitrogen. Groups attached to the carbonyl portion may be either carbon, hydrogen, nitrogen, oxygen, or sulfur. The sulfonyl analogs known have a carbon moiety attached to the sulfur.

The amine acylimides have been studied more intensively than the other three classes, and their infrared spectra, with absorption bands normally in the region 1550–1590  $\text{cm}^{-1}$ , support the resonance structures as shown.

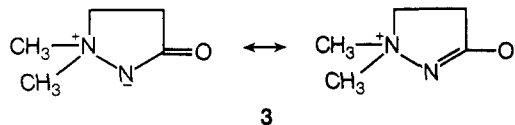


No previous survey of aminimides has been published, but this class of compounds is mentioned briefly in texts on nitrogen compounds<sup>1-4</sup> and reviews on quaternized hydrazine derivatives<sup>5</sup> and pyridinium ylides.<sup>6</sup>

The nomenclature for this class of compounds is varied; the majority of investigators use the aminimide nomenclature because they are isoelectronic with amine oxides. Thus **1** is called trimethylamine-*p*-toluenesulfonimide, and **2** is named trimethylamine-benzimide. Other investigators have used the names ammonium ylides or amidoammonium compounds. *Chemical Abstracts* in the Seventh Collective Index names this class as hydrazonium hydroxide inner salt. Compound **2** is indexed as hydrazonium, 2-benzoyl-1,1,1-trimethylhydroxide, inner salt.



Recently, several investigators have independently named these compounds by the IUPAC Nomenclature of Organic Chemistry (Section C, p 69). Structure **1** is *N*-trimethylammonio-*p*-toluenesulfonamidate, and **2** is *N*-trimethylammonio-benzamidate. This method fails, however, for cyclic aminimides such as **3**. The best name for



this type of compound is based on that used by *Chem-*

## I. Introduction

Aminimides are dipolar ions containing a cationic nitrogen bonded to an anion derived from a carboxamide,  $-\text{CONN}^+\equiv$ , sulfonamide,  $-\text{SO}_2\text{NN}^+\equiv$ , cyanamide,  $\text{N}^+\equiv\text{CN}^-\equiv$ , or nitroamide,  $\text{NO}_2\text{NN}^+\equiv$ . In all four structures, carbon substituents are attached to the quaternary

(1) J. Z. Zabicky, "The Chemistry of Amides," Interscience, New York, N. Y., 1970, pp 572–574.

(2) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 179.

(3) C. G. Overberger, J. P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press, New York, N. Y., 1966, p 79.

(4) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 266–270.

(5) H. H. Sisler, G. M. Omietanski, and B. Rudner, *Chem. Rev.*, **57**, 1021 (1957).

(6) T. Sasaki, *Kagaku Kogyo*, **23**, 504 (1972).

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ical Abstracts: 1,1-dimethyl-3-oxopyrazolinium hydroxide inner salt.

The aminimide nomenclature will be used in this review, when appropriate, since it is generally more informative than the IUPAC name and less cumbersome than the *Chemical Abstracts* methods.

The first aminimides were prepared in 1930 by Curtius by the reaction of sulfonyl azides with pyridine and were formulated incorrectly as 2-, 3-, and 4-aminopyridine derivatives. In 1947, it was shown that these compounds were aminimides. Investigations of this class of compound remained dormant until 1954 when syntheses of aminimides were devised from 1,1-dimethylhydrazine. This facile method of preparation avoids the use of azides and gave an impetus to industry to study aminimides which resulted in increased publications. This review summarizes the investigations which have appeared in *Chemical Abstracts* and well-known journals up to July 1972.<sup>6a</sup>

## II. Synthesis of Aminimides

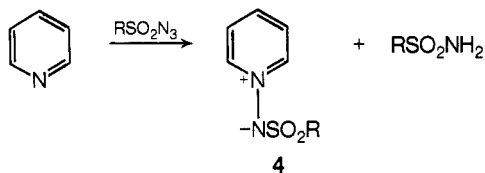
### A. General Methods

There are a number of related methods of general applicability which may be used for the preparation of most simple aminimides, and these are discussed in this section. More specialized methods which were used as proof of the structure are included in this section but those which lead to cyclic aminimides will be discussed in section II.B.

#### 1. Reaction of Acid Azides with Amines

##### a. Sulfonyl Derivatives

Sulfonyl azides react with pyridine derivatives to form the pyridine-1-sulfonimides **4**, the unsubstituted sulfonamides, and other products which will depend upon the substituents on the pyridine ring.



This reaction was carried out first by Curtius and coworkers and was reported to give, often in good yields, compounds which were formulated as 2-, 3-, or 4-aminopyridine derivatives.<sup>7-11</sup> Alamela and Ganapathi<sup>12</sup> reported that *p*-acetamidobenzenesulfonyl azide and pyridine gave 3-*p*-acetamidobenzenesulfonamidopyridine. It was later shown<sup>13,14</sup> that the product was actually pyridine-1-*p*-acetamidobenzenesulfonimide (**5**) whose structure was proven by hydrolysis with hydrochloric acid to 1-aminopyridinium chloride (**6**) and sulfanilic acid. 1-Aminopyridinium chloride (**6**), when treated with *p*-

(6a) Note Added in Proof. Since the acceptance of this publication, a review article on aminimides by H. J. Timpe has appeared in *Z. Chem.*, **12** (7), 250 (1972).

(7) T. Curtius, *J. Prakt. Chem.*, [2] **125**, 303 (1930).

(8) T. Curtius and J. Rissom, *J. Prakt. Chem.*, [2] **125**, 311 (1930).

(9) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, [2] **125**, 323 (1930).

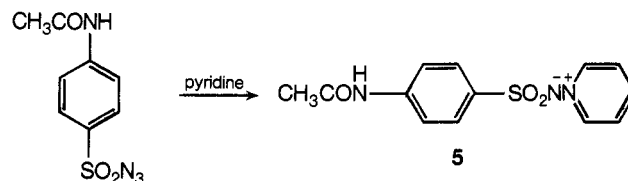
(10) T. Curtius and K. Vorbach, *J. Prakt. Chem.*, [2] **125**, 340 (1930).

(11) T. Curtius, H. Bottler, and W. Raudenbusch, *J. Prakt. Chem.*, [2] **125**, 380 (1930).

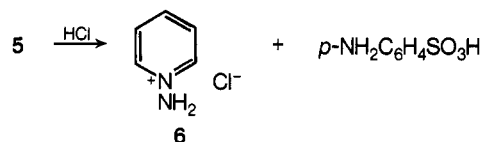
(12) B. S. Alamela and K. Ganapathi, *Current Sci.*, **12**, 119 (1943); *Chem. Abstr.*, **38**, 5492 (1944).

(13) J. N. Ashley, G. L. Buchanan, and A. P. T. Eason, *J. Chem. Soc.*, 60 (1947).

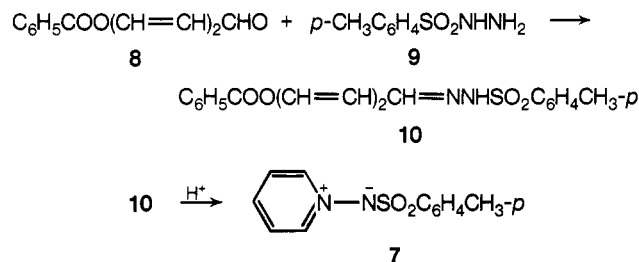
(14) P. K. Datta, *J. Indian Chem. Soc.*, **24**, 109 (1947).



acetamidossulfonyl chloride in the presence of sodium carbonate, gave the aminimide **5**.<sup>13</sup>



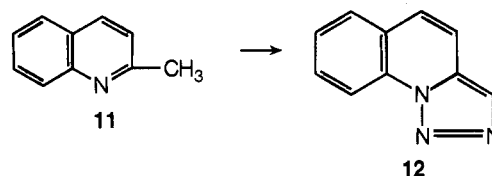
Further proof for the dipolar structure was the synthesis of pyridine-1-*p*-toluenesulfonimide (**7**) from glutamic dialdehyde monobenzoate (**8**) and *p*-toluenesulfonylhydrazide (**9**). The resulting hydrazone (**10**) upon treatment with hydrogen chloride in ethanol gave **7**.<sup>14</sup>



Treatment of 2- and 4-picoline, 2,6-lutidine, and 2,4,6-collidine with benzenesulfonyl azide gave in addition to the aminimide and benzenesulfonamide the corresponding 3-benzenesulfonamido derivatives as minor products (5-15%). The product from 2-picoline was a mixture of 3- and 5-benzenesulfonamido-2-methylpyridine.<sup>15</sup>

Quinoline and 3-methylisoquinoline behaved similarly and gave 8-benzenesulfonamidoquinoline (1%) and 4-benzenesulfonamido-3-methylisoquinoline (12.4%). Isoquinoline gave only benzenesulfonamide.

Quinaldine (**11**) behaved differently in this reaction and formed benzenesulfonamide and 1,2,3-triazolo[1,5-a]quinoline (**12**); identical behavior was shown by 1-methylisoquinoline and 6-methylphenanthridine.<sup>15</sup>



The reaction of arenesulfonyl azides with tertiary amines does not yield aminimides. Tributylamine and triethylamine gave with *p*-toluenesulfonyl azide only *p*-toluenesulfonamide (46%). Dimethylaniline, on the other hand, with benzenesulfonyl azide gave *p*-dimethylamino-benzenesulfonamide (22%). This product differed in melting point from that reported by Curtius<sup>7</sup> but was identical with a sample synthesized from *p*-dimethylaminoaniline and benzenesulfonyl chloride.<sup>16</sup> *p*-Acetamidobenzenesulfonyl azide is reported to form an aminimide with *N,N*-dimethylaniline; no proof of structure was offered for this compound.<sup>17</sup>

Chloramine T which converts sulfides into the sulfur analogs of aminimides does not react with dimethylaniline<sup>18</sup> or ethyl-*n*-butylamine.<sup>16</sup>

(15) R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, **37**, 2022 (1972).

(16) J. Chua, Ph.D. Thesis, University of Iowa, 1959.

(17) F. J. W. Cremlyon, *J. Chem. Soc.*, 1132 (1965).





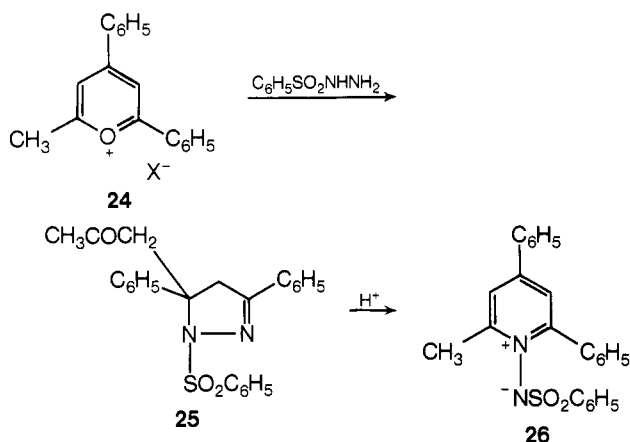
TABLE III. Aminimides,  $R_3\overset{+}{N}\overset{-}{N}SO_2R'$ , Prepared from Sulfonylhydrazides

$R_3N$	$R'$	Yield, % <sup>a</sup>	Mp, °C	Ref
$(CH_3)_3N$	$p\text{-CH}_3C_6H_4$	55	175–176	31
$(CH_3)_2NCH_2C_6H_5$	$p\text{-CH}_3C_6H_4$	46.5, 60	176–177	32
$(CH_3)_2NCH_2C\equiv CHCH_3$	$p\text{-CH}_3C_6H_4$	74.4	136–138	32
$(CH_3)_3N$	$C_{12}H_{25}$	90	133–134	33
$(CH_3)_2NC_{12}H_{25}$	$CH_3$		83–84 <sup>b</sup>	33
1-Methyl-1,2,4-triazole	$C_6H_5^c$	37	197	34
1-Benzyl-1,2,4-triazole	$C_6H_5^c$	40	202	34
1- <i>p</i> -Chlorobenzyl-1,2,4-triazole	$C_6H_5^c$	54	186	34
1- <i>p</i> -Chlorobenzyl-1,2,4-triazole	$p\text{-CH}_3C_6H_4^c$	70	212	34

<sup>a</sup> Overall yield from hydrazide. <sup>b</sup> Dihydrate. <sup>c</sup> Sulfonylimide is present in the 4-position of the triazole.

fonimide (**23**).<sup>35</sup> The intermediate in this reaction is probably 5-(2,4-dinitroanilino)-2-carbamoyl-2,4-pentadienal *N-p*-toluenesulfonylhydrazide (see ref 136).

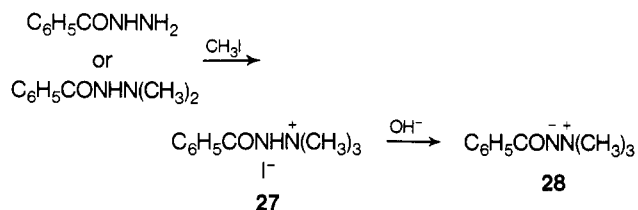
Benzenesulfonylhydrazide reacts with pyrylium salts (**24**) to form 2-pyrazolines (**25**), which in one case was made to rearrange by perchloric acid in acetic acid into 2,4-diphenyl-6-methylpyridine-1-benzenesulfonimide (**26**).<sup>36</sup>



The same reaction with 2,4,6-trimethylpyrylium perchlorate and benzenesulfonylhydrazide followed by treatment with alkali is reported to give 2,4,6-trimethylpyridine-1-benzenesulfonimide directly.<sup>15</sup> 2,4,6-Triphenylpyrylium salts did not react under these conditions.

#### b. Acyl Derivatives

Many acylaminimides have been prepared from acylhydrazides by reactions similar to those used for the sulfonyl derivatives.<sup>37</sup> The dialkylhydrazides necessary



for this preparation are best prepared by the action of an acid chloride<sup>38</sup> or anhydride on a 1,1-disubstituted hydrazide.<sup>39</sup>

(35) J. Epszajn, E. Lunt, and A. R. Katritzky, *Tetrahedron*, **26**, 1665 (1970).

(36) M. Lempert-Streter and K. Lempert, *Acta Chim. (Budapest)*, **65**, 443 (1970).

(37) R. L. Hinman and M. C. Flores, *J. Org. Chem.*, **24**, 660 (1959).

(38) E. A. Sedor, R. E. Freis, and H. J. Richards, *Org. Prep. Proced.*, **2**, 275 (1970).

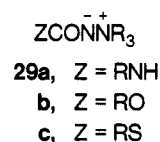
Direct hydrazinolysis of esters with dimethylhydrazine occurs only with formates; other esters of aliphatic or aromatic acids<sup>40</sup> do not react.

The hydrazinolysis of aromatic esters with 1,1-dialkylhydrazines, when catalyzed by sodium hydride or sodium methoxide, gave hydrazides in yields which varied from 14 to 80%.<sup>41</sup>

Hydrazides have also been obtained from 1,1-dimethylhydrazine and 1-aminopiperidine and aromatic acids in yields varying from 23 to 68% by using dicyclohexylcarbodiimide as the dehydrating agent.<sup>41</sup> This reaction can be carried out more simply by heating acids with 1,1-dimethylhydrazine in a solvent under pressure at 150° for 24 hr;<sup>42</sup> yields of 60–80% are reported.

Akylation in the second step can be carried out using alkyl halides or alkyl *p*-toluenesulfonates. The ease with which this step occurs will depend on the size of the alkyl group.<sup>37</sup> The aminimides prepared by this method are listed in Table IV.

Hydrazides prepared from unsymmetrically substituted hydrazines and isocyanates, chloroformates, and chlorothioformates have been converted to aminimides (**29**) by



(39) S. Wawzonek and E. Yeakey, *J. Amer. Chem. Soc.*, **82**, 5718 (1960).

(40) R. L. Hinman and D. Fulton, *J. Amer. Chem. Soc.*, **80**, 1895 (1958).

(41) R. F. Smith, A. C. Bates, A. J. Battisti, P. G. Byrnes, C. T. Mroz, T. J. Smearing, and F. X. Albrecht, *J. Org. Chem.*, **33**, 851 (1968).

(42) R. E. Freis, R. A. Grimm and W. J. McKillip, *J. Amer. Oil Chem. Soc.*, **49**, 111 (1972).

(43) H. P. Benecke, Ph.D. Thesis, University of Cincinnati, 1969.

(44) M. S. Gibson, P. D. Callaghan, R. F. Smith, A. C. Bates, J. R. Davidson, and A. J. Battisti, *J. Chem. Soc. C*, 2577 (1967).

(45) R. C. Slagel and A. E. Bloomquist, *Can. J. Chem.*, **45**, 2625 (1967).

(46) T. A. Sokolova, L. A. Ovsyannikova, and N. P. Zapevalova, *Zh. Org. Khim.*, **2**, 818 (1966).

(47) L. A. Ovsyannikova, T. A. Sokolova, and N. P. Zapevalova, *Zh. Org. Khim.*, **4**, 459 (1968).

(48) W. J. McKillip, L. M. Clemens, and R. Haugland, *Can. J. Chem.*, **45**, 2613 (1967).

(49) B. M. Culbertson, E. A. Sedor, R. Freis, and S. Dietz, *J. Polym. Sci., Part A-1*, **6**, 2197 (1968).

(50) E. Kameyama, Y. Minegishi, and T. Kuwamura, *Yukagaku*, **18**, 897 (1969).

(51) H. P. Benecke and J. H. Wikel, *Tetrahedron Lett.*, 289 (1972).

(52) S. Wawzonek, J. Chua, E. L. Yeakey, and W. J. McKillip, *J. Org. Chem.*, **28**, 2376 (1963).

(53) M. S. Gibson and I. D. Brindle, *Chem. Commun.*, 803 (1969).

(54) J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Commun.*, 31 (1970).

(55) D. G. Morris, B. W. Smith, and R. J. Wood, *Chem. Commun.*, 1134 (1968).

(56) S. Wawzonek and E. E. Paschke, *J. Org. Chem.*, **36**, 1474 (1971).

TABLE IV. Aminimides,  $R_3\overset{\oplus}{N}\overset{\ominus}{N}COR'$ , Prepared from Acylhydrazides

$R_3N$	$R'$	Yield, % <sup>a</sup>	Mp, °C	Ref
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>3</sub>		122.5–123	43
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>6</sub> H <sub>5</sub>	48	167–169	37
(CH <sub>3</sub> ) <sub>3</sub> N	<i>m</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	71	108–112	44
(CH <sub>3</sub> ) <sub>3</sub> N	4-Pyridyl	40	191–192	37
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>2</sub> =C(CH <sub>3</sub> )–	96	149–150	45
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>2</sub> =C(CH <sub>3</sub> )–	70 <sup>d</sup>	146–147	46
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>3</sub> CH=CH	71	171–172	46
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>2</sub> =CH	93	102–104	45
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>2</sub> =CH	71	100–101	47
(CH <sub>3</sub> ) <sub>3</sub> N	(CH <sub>3</sub> ) <sub>2</sub> CH	50	112–112.5	46
(CH <sub>3</sub> ) <sub>3</sub> N	(CH <sub>2</sub> ) <sub>7</sub> <sup>b</sup>	43	146–147.5	48
(CH <sub>3</sub> ) <sub>3</sub> N	(CH <sub>2</sub> ) <sub>8</sub> <sup>b</sup>	56	142–144	48
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>2</sub> CH– <sup>b,c</sup>	60	177–179	48
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>2</sub> CH–			
(CH <sub>3</sub> ) <sub>3</sub> N	<i>m</i> -C <sub>6</sub> H <sub>4</sub> <sup>b</sup>	92	251	48
(CH <sub>3</sub> ) <sub>3</sub> N	2,2,4-Trimethyl-3-ketobutyl	83	121–121.5	48
(CH <sub>3</sub> ) <sub>3</sub> N	<i>p</i> -CH <sub>2</sub> =CHC <sub>6</sub> H <sub>4</sub>	64	122–124	49
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>11</sub> H <sub>23</sub>	80	53–54	50
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>13</sub> H <sub>27</sub>	73	63.5–64.5	50
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>17</sub> H <sub>35</sub>	73	79	50
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	50	87–88 (picrate)	39
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH			51
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>3</sub> C			51
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	CH <sub>3</sub>	73	175–177	39
CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )NCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	CH <sub>3</sub>	77	126–127	52
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH=CH <sub>2</sub>	CH <sub>3</sub>			53
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH=CH-CH <sub>3</sub>	CH <sub>3</sub>			54
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>			54
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>			54
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>			54
(CH <sub>3</sub> ) <sub>2</sub> N-cyclooctyl	CH <sub>3</sub>			55
(CH <sub>3</sub> ) <sub>2</sub> NCH(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>			55
CH <sub>3</sub> N(C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	CH <sub>3</sub>	68	Oil	56
CH <sub>3</sub> N(C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	48	Oil	56
1-Methyl-2-phenylpyrrolidine	CH <sub>3</sub>	68	Oil	57
1-Methyl-2-phenylpiperidine	CH <sub>3</sub>	55	150.5–152	58
1-Methylpiperidine	C <sub>6</sub> H <sub>5</sub>	70	121–123	44
(CH <sub>3</sub> ) <sub>3</sub> N	Dimer acid <sup>e</sup>	86	Oil	42

<sup>a</sup> Overall yield from hydrazide. <sup>b</sup> Bis(aminimide). <sup>c</sup> *trans*. <sup>d</sup> From methiodide. <sup>e</sup> Emery Empol 1010 (Emery Corp. trademark).

TABLE V. Aminimides, ZCON<sup>+</sup>NR<sub>3</sub>

$R_3N$	Z	Yield, % <sup>a</sup>	Mp, °C	Ref
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>6</sub> H <sub>5</sub> NH	53	205	59
(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>3</sub> NH	53	134–138	59
(CH <sub>3</sub> ) <sub>3</sub> N	$\alpha$ -Naphthylamino	49	176–177	60
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )N	8.5	106–107	60
(CH <sub>3</sub> ) <sub>3</sub> N	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> N	51	182 dec	60
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>6</sub> H <sub>5</sub> O	55	100–102	
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>2</sub> H <sub>5</sub> O	50	95–98	59
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>6</sub> H <sub>5</sub> S	36	83–85	59
(CH <sub>3</sub> ) <sub>3</sub> N	C <sub>2</sub> H <sub>5</sub> S	35	82–84	59
1-Methyl-2-phenylpiperidine	C <sub>2</sub> H <sub>5</sub> O	41	104	58

<sup>a</sup> Overall yield from hydrazide.

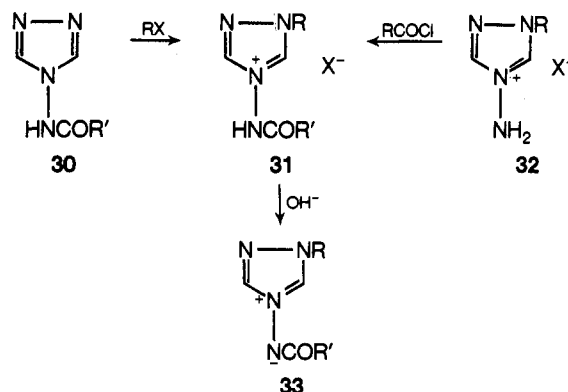
this method.<sup>59</sup> Examples of aminimides prepared by this method are given in Table V.

(57) S. Wawzonek and R. C. Gueldner, *J. Org. Chem.*, **30**, 3031 (1965).

(58) S. Wawzonek and J. G. Stephanie, *J. Org. Chem.*, **36**, 2467 (1971).

(59) M. S. Brown, *J. Chem. Eng. Data*, **12**, 612 (1967).

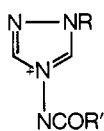
1-Alkyl-1,2,4-triazole-4-acylimides (**33**) have been prepared by the sequence of reactions shown.<sup>61</sup> Examples prepared in this manner are given in Table VI.



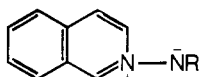
Aminimides (**35**) derived from isoquinoline have been synthesized from the complex reaction of 2-(2,4-dinitro-

(60) S. Wawzonek, T. H. Plaisance, and D. P. Boaz, *Tetrahedron*, **28**, 3669 (1972).

(61) H. G. O. Becker, N. Sauder, and H. J. Timpe, *J. Prakt. Chem.*, **311**, 897 (1969).

TABLE VI. 1-Alkyl-1,2,4-triazole-4-acylimides<sup>61</sup>

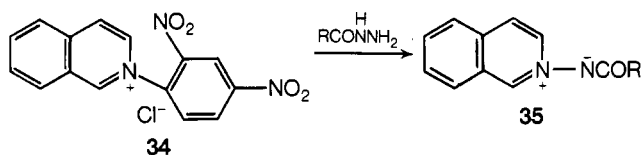
R	R'	Yield, %	Mp, °C
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>3</sub>	87	188
<i>p</i> -ClC <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>3</sub>	87	221
C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	82	156
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	H	70	163
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub>	CH <sub>3</sub>	91	206
<i>p</i> -BrC <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub>	CH <sub>3</sub>	92	230
$\alpha$ -Naphthylmethyl	CH <sub>3</sub>	81	175
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	78	185
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	93	193
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	83	166

TABLE VII. Isoquinoline-2-acylimides.<sup>62</sup>

R	Yield, %	Mp, °C
NH <sub>2</sub> COCO	86	28
C <sub>6</sub> H <sub>5</sub> CO	100	188
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CO	42	218
COOC <sub>2</sub> H <sub>5</sub>	83	132
CONH <sub>2</sub>	84	175
CSNH <sub>2</sub>	98	147-148
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	97	228-229
CN	10	147

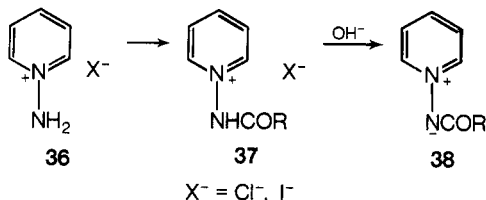
phenyl)isoquinolinium chloride (**34**) and acylhydrazides.<sup>62</sup>

Examples of aminimides prepared in this manner or from the reacylation of the carbethoxy compound (see section III.H) are given in Table VII.



### 3. Preparation from Hydrazinium Salts

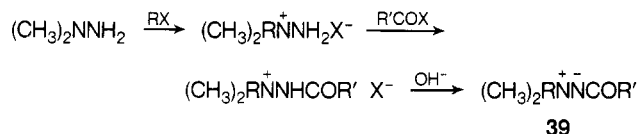
1-Aminopyridinium halides (**36**) when treated with acetic anhydride or benzoyl chloride form the corresponding acylamino derivatives (**37**) which with alkali gave the aminimide **38**.<sup>21</sup> The 1-aminopyridinium halides (**36**) used in this reaction are prepared by treating pyridine first with hydroxylamine-*O*-sulfonic acid and then with hydriodic acid<sup>63</sup> or concentrated hydrochloric acid.<sup>35</sup> The latter salt cannot be made by the reaction of chloramine and pyridine.



(62) B. Agai and K. Lempert, *Tetrahedron*, **28**, 2069 (1972).

(63) R. Gosl and A. Meuwsen, *Chem. Ber.*, **92**, 2521 (1959).

Trialkylamine-acylimides (**39**) have been synthesized in a similar fashion from 1-alkyl-1,1-dimethylhydrazinium halides.<sup>64,65</sup>



Examples of aminimides prepared by this method are given in Table VIII.

TABLE VIII. Aminimides, R<sub>3</sub>N<sup>+</sup>NCOR'

Amine	R'	Yield, % <sup>a</sup>	Mp, °C	Ref
Pyridine	CH <sub>3</sub>	83	168	22
Pyridine	C <sub>6</sub> H <sub>5</sub>	81	177.5	22
Pyridine	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	86	145	66
Pyridine	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	81	164-166	66
Pyridine	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	88	87-88	66
Pyridine	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	82	104	66
Pyridine	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	80	186-187	66
Pyridine	C <sub>6</sub> H <sub>5</sub> CH=CH	90	149-150	66
Pyridine	C <sub>4</sub> H <sub>3</sub> SCH=CH <sup>c</sup>	87	125-126	66
Pyridine	C <sub>4</sub> H <sub>3</sub> O <sup>d</sup>	78	223-224	66
Pyridine	C <sub>4</sub> H <sub>3</sub> S <sup>c</sup>	91	208-209	66
2-Methylpyridine	CH <sub>3</sub>	83	167 <sup>b</sup>	67
4-Methylpyridine	CH <sub>3</sub>		166 <sup>b</sup>	67
2-Ethylpyridine	CH <sub>3</sub>		163 <sup>b</sup>	67
2-Methylpyridine	CH <sub>3</sub>	76.5	166-167	28
3,5-Dimethylpyridine	CH <sub>3</sub>		175	67
2,4,6-Trimethylpyridine	CH <sub>3</sub>		84	67
C <sub>6</sub> H <sub>13</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>19</sub>	7		65
C <sub>9</sub> H <sub>17</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>5</sub> H <sub>11</sub>	33	42-42.5	65
C <sub>9</sub> H <sub>17</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>7</sub> H <sub>15</sub>	15	39-41	65
C <sub>9</sub> H <sub>17</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>19</sub>	17	46.5-48	65
C <sub>10</sub> H <sub>21</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>19</sub>	11	43	65
C <sub>12</sub> H <sub>25</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>19</sub>	29	41.5-42	65
C <sub>12</sub> H <sub>25</sub> (CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	60	39-40	33
C <sub>10</sub> H <sub>21</sub> N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	47		64
C <sub>12</sub> H <sub>25</sub> N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	78	39-40	64
C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	89	54-57	64
C <sub>18</sub> H <sub>37</sub> N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	68	61-62	64

<sup>a</sup> Overall yield from hydrazinium salt. <sup>b</sup> Picrate. <sup>c</sup> C<sub>4</sub>H<sub>3</sub>S = 2-thienyl. <sup>d</sup> C<sub>4</sub>H<sub>3</sub>O = 2-furyl.

The preparation of aminimides **38** can be carried out in one step by treating the 1-aminopyridinium halide (**36**) with an anhydride or acid chloride in the presence of base or sodium carbonate. The intermediate in this reaction is probably like the aminimine **41** (see section II.A.4) and not the 1-acylamino pyridinium halide (**37**). Such an intermediate (**41**) is not stable in the quinoline series but dimerizes to **42**. 1-Aminoquinolinium iodide (**40**), for example, when treated with alkali in dimethylformamide, gave the dimer (**42**) of the aminimine **41**. The dimer (**42**) upon treatment with alkali and acetic anhydride forms quinoline-1-acetamide (**43**) which is also obtained from **40** by successive treatments with acetic anhydride and alkali.<sup>68</sup>

(64) E. Kameyama, Y. Minnegishi, and T. Kuwamura, *Kogyo Kagaku Zasshi*, **71**, 1671 (1968); *Chem. Abstr.*, **70**, 46787k (1969).

(65) E. Kameyama, Y. Minnegishi, and T. Kuwamura, *ibid.*, **73**, 1018 (1970); *Chem. Abstr.*, **72**, 45292z (1970).

(66) J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **50**, 584 (1972).

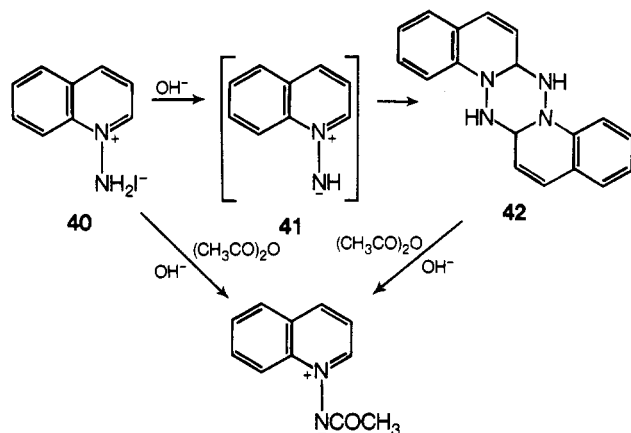
(67) T. Okamoto, M. Hirobe, and A. Ohsawa, *Chem. Pharm. Bull.*, **14**, 518 (1966).

(68) T. Okamoto, M. Hirobe, and T. Yamazaki, *Chem. Pharm. Bull.*, **14**, 512 (1966).

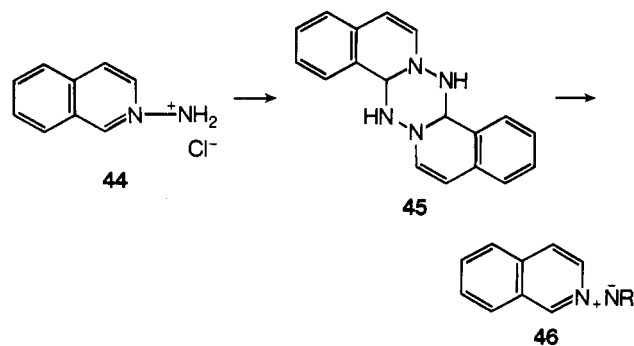
TABLE IX. Aminimides, R<sub>3</sub>N- $\bar{N}$ R'

Amine	R'	Yield, %	Mp, °C	Ref
Pyridine	COOC <sub>2</sub> H <sub>5</sub>	48	108-109	21
2-Methylpyridine	COOC <sub>2</sub> H <sub>5</sub>	41	108-109	69
		47 <sup>a</sup>	141-142 <sup>b</sup>	21
		78	145-147 <sup>b</sup>	69
4-Methylpyridine	COOC <sub>2</sub> H <sub>5</sub>	29	141.5-142.5	21
		60	148-151	69
3-Methylpyridine	COOC <sub>2</sub> H <sub>5</sub>	44	141-143	69
2,4-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	63	Oil	69
2,5-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	34	Solid	69
2,6-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	49 <sup>b</sup>	101-102	21
		43	Solid <sup>c</sup>	69
3,4-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	46	154-155	69
3,5-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	51	138-140	21
		45	132-134	69
2,4,6-Trimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	14	137-140	69
4-Dimethylaminopyridine	COOC <sub>2</sub> H <sub>5</sub>	53	201.5-202.5	21
Pyridine	C <sub>6</sub> H <sub>5</sub> CO	83	179-180.5	21
		90	179-180	35
Pyridine	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub>	62	153.3-154.5	35
Pyridine	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	57	215-217	21
Pyridine	<i>p</i> -CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	46	295-300	13
Pyridine	2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> SO <sub>2</sub>	23	202-203	35
Quinoline	CH <sub>3</sub> CO	45 <sup>d</sup>	89-90	68
Isoquinoline	CN	75 <sup>d</sup>	147	62
Isoquinoline	C <sub>6</sub> H <sub>5</sub> NHCO	61 <sup>d</sup>	168	62
Isoquinoline	C <sub>6</sub> H <sub>5</sub> NHCS	75 <sup>d</sup>	164	62
Pyridazine	CH <sub>3</sub> CO	72	125-127	70
Pyridazine	C <sub>6</sub> H <sub>5</sub> CO	87.5	156-157	70
3-Methoxypyridazine	CH <sub>3</sub> CO	79.4	136-137	70
3-Methoxypyridazine	C <sub>6</sub> H <sub>5</sub> CO	91.4	169-169.5	70

<sup>a</sup> Yield of picrate. <sup>b</sup> Picrate. <sup>c</sup> Hygroscopic. <sup>d</sup> From dimer.



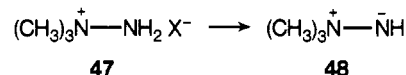
2-Aminoisoquinolinium chloride (44) gave a similar dimer (45) which when treated with either phenyl isocyanate, phenyl isothiocyanate, or cyanogen bromide gave the corresponding aminimides 46 (R = C<sub>6</sub>H<sub>5</sub>NHCO,



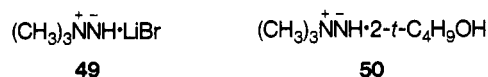
C<sub>6</sub>H<sub>5</sub>NHCS, CN).<sup>62</sup> Table IX lists examples made by this reaction.

#### 4. Preparation from Trialkylaminimines, R<sub>3</sub>N<sup>+</sup>-NH<sup>-</sup>

1,1,1-Trimethylhydrazinium halides (47) when treated with a strong base such as phenyllithium in ether,<sup>71</sup> potassium amide in liquid ammonia, or potassium *tert*-butoxide in *tert*-butyl alcohol and tetrahydrofuran form trimethylaminimine (48).<sup>72</sup> The product from the second



method is the parent compound which is hygroscopic and unstable. The other two methods give the aminimine coordinated with lithium bromide (49) and 2 mol of *tert*-butyl alcohol, respectively (50).



The dialcoholate 50 is a very strong base and reacts with acid chlorides, *p*-toluenesulfonyl chloride, and isocyanates and forms the aminimides shown in Table X.<sup>72</sup> The aminimine if generated in solution in the presence of esters converts these compounds into aminimides. This

(69) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970).

(70) Y. Kobayashi, T. Kutsuma, and K. Morinaga, *Chem. Pharm. Bull.*, **19**, 2106 (1971).

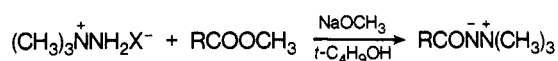
(71) G. Wittig and M. Rieber, *Justus Liebig's Ann. Chem.*, **562**, 177 (1949).

(72) R. Appel, H. Heinen, and R. Schoelhorn, *Chem. Ber.*, **99**, 3118 (1966).

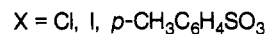


TABLE X. Aminimides,  $(\text{CH}_3)_3\text{N}^+\text{NR}$ 

R	Yield, %	Mp, °C
CH <sub>3</sub> CO	80	122-123
C <sub>6</sub> H <sub>5</sub> CO	75	169
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCO	83	273
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	74	173
C <sub>6</sub> H <sub>5</sub> NHCO	92	226
C <sub>2</sub> H <sub>5</sub> NHCO	75	124-126



53



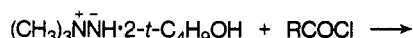
and esters of oleic, linoleic, phenylstearic, ricinoleic, and *threo*-9,10-dihydroxystearic acids.<sup>42</sup> Examples of aminimides prepared by this method are given in Table XI.

This reaction has been extended to the preparation of 1,1-dimethyl-1-phenylamine-2-benzoylimide (13%, mp

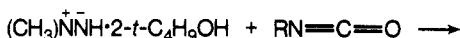
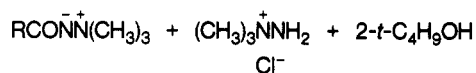
TABLE XI. Aminimides,  $\text{RCO}\text{N}^+\text{N}(\text{CH}_3)_3$ 

R	Yield, % <sup>a</sup>	Mp, °C	Ref
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> -	95	53-54	74
Adamantyl	63.5	174-175	74
Cyclohex-4-ene-1,2-diyl	63	Oil <sup>c</sup>	74
C <sub>6</sub> H <sub>5</sub>	90.3	169-170	74
3-Pyridyl	94	110-112	74
CF <sub>3</sub> CF <sub>2</sub> -	100	104-107	74
CH <sub>2</sub> =C(CH <sub>3</sub> )-	91	149-150	45, 75
CH <sub>2</sub> =CH-	35 <sup>b</sup>	102-104	45
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> -	82	77-79	42
Dimer acid <sup>d</sup>	85	Oil	42
CH <sub>2</sub> =C(CH <sub>3</sub> )CON(C-C <sub>6</sub> H <sub>11</sub> )CH <sub>2</sub> CH <sub>2</sub>	60	144-146	77
CH <sub>2</sub> =C(CH <sub>3</sub> )CON(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>2</sub>	100	164-166	77
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CONHCH <sub>2</sub>	100	84-85	77
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CONHCH <sub>2</sub> CH <sub>2</sub>	55	86-87	77
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NHCH <sub>2</sub> CH <sub>2</sub>	85	34-38	78
CH <sub>2</sub> =CHCH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub>	93	Liquid	78
C <sub>6</sub> H <sub>5</sub> NHCH <sub>2</sub> CH <sub>2</sub>	83	125.5-126.5	78
3-ClC <sub>6</sub> H <sub>4</sub> NHCH <sub>2</sub> CH <sub>2</sub>	84	98-99	78
3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NHCH <sub>2</sub> CH <sub>2</sub>	81	100.5-101.5	78
2-Furfuryl-NHCH <sub>2</sub> CH <sub>2</sub>	94	Liquid	78
3-Picolyl-NHCH <sub>2</sub> CH <sub>2</sub>	100	Liquid	78
2-Pyridinoethyl-NHCH <sub>2</sub> CH <sub>2</sub>	94	94-95	78

<sup>a</sup> Crude yield. <sup>b</sup> Pure compound. <sup>c</sup> Monoaminimide. <sup>d</sup> Emery Empol 1010.



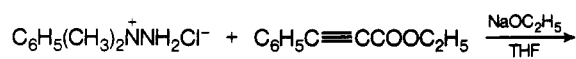
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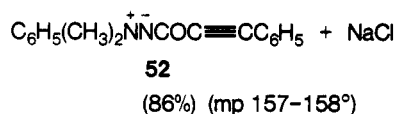
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reaction was first carried out using 1,1-dimethyl-1-phenylhydrazinium chloride (51) and ethyl phenylpropiolate,<sup>73</sup>



51



and then developed into a general method using 1,1,1-trimethylhydrazinium salts (53) by McKillip and Slagel<sup>74</sup> (Table XI). This reaction works satisfactorily with methyl acrylate, methyl methacrylate,<sup>45,73,75</sup>  $\gamma$ -butyrolactone,<sup>76</sup>

(73) H. W. Schiessl and R. Appel, *J. Org. Chem.*, **31**, 3851 (1966).

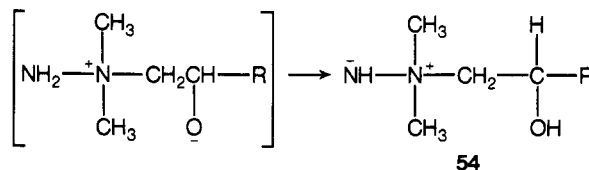
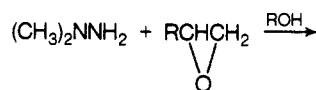
(74) W. J. McKillip and R. C. Slagel, *Can. J. Chem.*, **45**, 2619 (1967).

(75) B. M. Culbertson and R. C. Slagel, *J. Polym. Sci., Part A-1*, **6**, 363 (1968).

(76) L. M. Clemens, W. J. McKillip, and E. A. Sedor, U. S. Patent 3,499,032; *Chem. Abstr.*, **72**, 325 (1970).

158-159°) from ethyl benzoate and 1,1-dimethyl-1-phenylhydrazinium hydrosulfate,<sup>79</sup> and 1-methyl-2-phenylpiperidine-1-carbomethoxyimide (28%) from 1-amino-1-methyl-2-phenylpiperidinium iodide and ethyl carbonate.<sup>58</sup>

The discovery that epoxides react with 1,1-dimethylhydrazine in polar solvents such as alcohols and form 1,1-dimethyl-1-( $\beta$ -hydroxyalkyl)aminimines (54) has been made the basis of an important synthesis of aminimides.<sup>80,81</sup> This reaction if carried out in the presence of an ester yields the aminimide. Examples synthesized in this manner are listed in Table XII.



(77) B. M. Culbertson, R. E. Freis, and D. Grote, *J. Polym. Sci., Part A-1*, **9**, 343 (1971).

(78) D. Aelony and W. J. McKillip, *J. Heterocycl. Chem.*, **9**, 687 (1972).

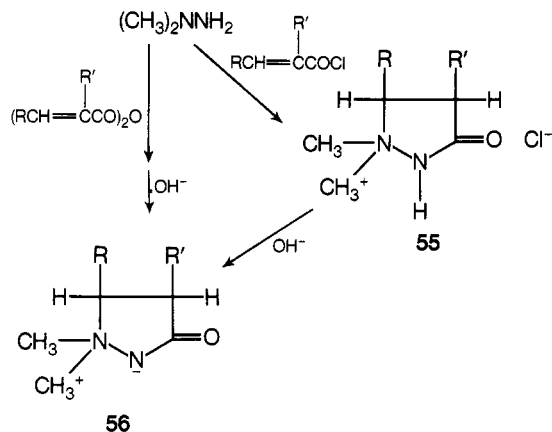
(79) S. Wawzonek and E. E. Paschke, *Org. Prep. Proced.*, **3**, 209 (1971).

(80) R. C. Slagel, *J. Org. Chem.*, **33**, 1374 (1968).

(81) B. M. Culbertson, E. A. Sedor, and R. C. Slagel, *Macromolecules*, **1**, 254 (1968).

## B. Miscellaneous Syntheses

The reaction of 1,1-dimethylhydrazine with  $\alpha,\beta$ -unsaturated acid anhydrides and acid chlorides formed, besides a small amount of the dimethylhydrazides, the cyclic aminimides **56**.<sup>83-86</sup>

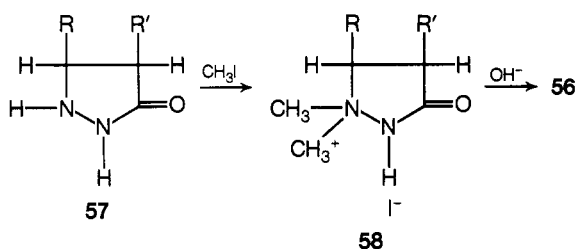


- a**, R = R' = H (mp 197–198°)  
**b**, R = H; R' = CH<sub>3</sub> (mp 237–238°)  
**c**, R = CH<sub>3</sub>; R' = H (mp 223–224°)

1,1-Dimethylhydrazine hydrochloride can be substituted for the free base in the reaction with the acid chlorides; however, no reaction was observed with methacrylic anhydride.<sup>87</sup> 1-Benzyl-1-phenylhydrazine in these reactions gave only the hydrazide of the acids.<sup>88</sup>

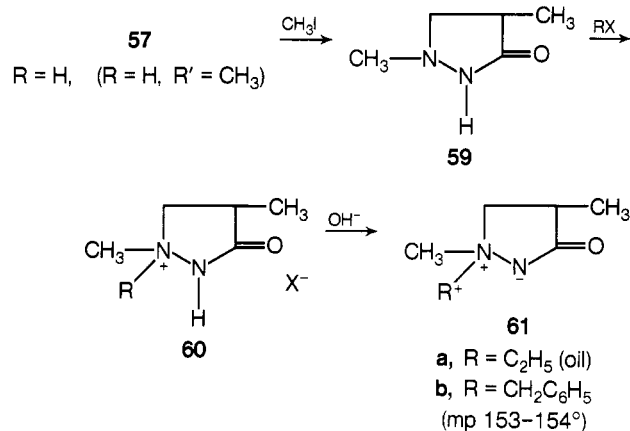
The cyclic aminimides **56** have also been prepared by treating the methyl esters of the acids with 1,1-dimethylhydrazine in water or alcohol. Methyl acrylate gave a 90–96% yield of **56a**, and methyl methacrylate gave a 5–10% yield of **56b**. The use of benzene as a solvent or heating the two components without a solvent formed the methyl  $\beta$ -(*N,N*-dimethyl)hydrazinopropionate.<sup>89</sup>

The 1,1-dimethyl-3-oxopyrazolinium hydroxide inner salt (**56**) structure was demonstrated by the nmr spectrum<sup>90</sup> and synthesis from the corresponding 3-pyrazolidone (**57**).



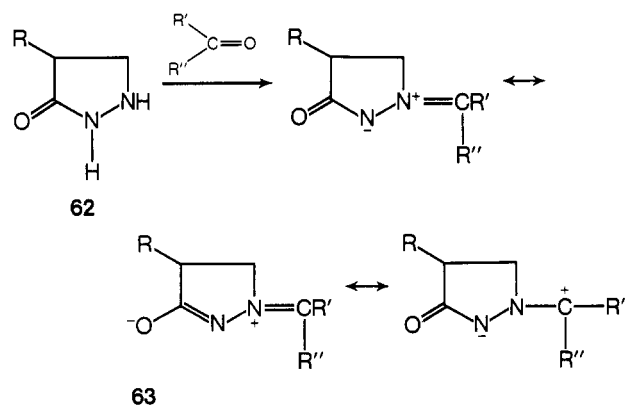
Stepwise alkylation of **57** (R = H; R' = CH<sub>3</sub>) with methyl iodide followed by either ethyl iodide<sup>85</sup> or benzyl

chloride<sup>86</sup> gave the cyclic aminimide **61**. The yields of **59** from **57** varied from 90 to 93% and that of the conversion of **59** to the cyclic aminimides **61** from 30 to 40%.

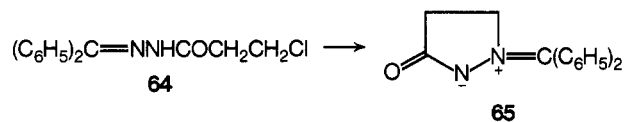


These aminimides (**56**) are converted thermally into the 1,1-dimethylhydrazide of the  $\alpha,\beta$ -unsaturated acids,<sup>47,86</sup> which have been used as starting materials for the aminimides of  $\alpha,\beta$ -unsaturated acids<sup>47</sup> (see section II.A.2.b). The intermediate 1,1,1-trimethyl-2-acroylhydrazonium iodide on heating at 130° gave the 2-methyl derivative of **58** (R = R' = H).<sup>91</sup>

3-Pyrazolidones (**62**) can also be converted by aldehydes and ketones into the cyclic aminimides **63**,<sup>92-95</sup> which are analogous in structure to the pyridine-1-acylimides. Examples prepared by this method from 3-pyrazolidone (**62**, R = H) are given in Table XIII. The product from 4-methyl-3-pyrazolidone and benzaldehyde (**63**, R = CH<sub>3</sub>; R' = H; R'' = C<sub>6</sub>H<sub>5</sub>) has been made and is reported to melt at 139–141°. Condensation of 5-phenyl-3-pyrazolidone and its *m*-nitro derivative (**62**, R = Ar) with benzaldehyde gave **63** (R = Ar; R' = H; R'' = C<sub>6</sub>H<sub>5</sub>)<sup>92</sup> in yields of 100 and 72% and melting at 200–201 and 206.5°, respectively.<sup>92</sup>



The same type of compound (**65**) is formed by treating the  $\beta$ -chloropropionylhydrazone of benzophenone (**64**)



(82) German Patent 1,965,989 (1971); *Chem. Abstr.*, **74**, 125730 (1971).

(83) T. A. Sokolova, A. I. Koltsov, N. P. Zapevalova, and L. A. Ovsyannikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1727 (1964).

(84) N. P. Zapevalova and T. A. Sokolova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1442 (1965).

(85) N. P. Zapevalova and T. A. Sokolova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 865 (1966).

(86) W. S. Wadsworth, Jr., *J. Org. Chem.*, **31**, 1704 (1966).

(87) N. P. Zapevalova, L. A. Ovsyannikova, and T. A. Sokolova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 162 (1967).

(88) N. P. Zapevalova and T. A. Sokolova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2197 (1966).

(89) N. P. Zapevalova, L. A. Ovsyannikova, and T. A. Sokolova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2200 (1966).

(90) A. I. Kaltsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1350 (1965).

(91) T. A. Sokolova and I. N. Osipova, *Dokl. Akad. Nauk SSSR*, **193**, 359 (1970).

(92) W. O. Godtfredsen and S. Vangedal, *Acta Chem. Scand.*, **9**, 1498 (1955).

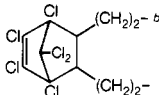
(93) H. Dorn and A. Otto, *Angew. Chem., Int. Ed. Engl.*, **7**, 214 (1968).

(94) H. Dorn and A. Otto, *Chem. Ber.*, **101**, 3287 (1968).

(95) H. Dorn and A. Otto, *Z. Chem.*, **8**, 273 (1968).

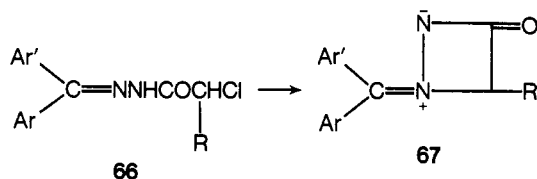
(96) H. Dorn and A. Otto, *Angew. Chem., Int. Ed. Engl.*, **7**, 885 (1968).

TABLE XII. Aminimides,  $R'CO\ddot{N}N^+(CH_3)_2CH_2C(OH)HR$ 

R'	R	Yield, %	Mp, °C	Ref
CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub>	96	108.5–110	80
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub>	CH <sub>3</sub>	100	48–50	80
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	62	51.5–54.4	80
CF <sub>3</sub>	CH <sub>3</sub>	89	109–110	80
CF <sub>3</sub> CF <sub>2</sub>	CH <sub>3</sub>	91	101–102	80
CH <sub>2</sub> =C(CH <sub>3</sub> )	CH <sub>3</sub>	98	146.5–147.5	80
CH <sub>2</sub> =C(CH <sub>3</sub> )	H	88	78–80	80
CH <sub>2</sub> =C(CH <sub>3</sub> )	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	100	64–66	80
CH <sub>2</sub> =C(CH <sub>3</sub> )	CH <sub>3</sub>	95	93–95	80
CH <sub>2</sub> =C(CH <sub>3</sub> )	CH <sub>2</sub> OH	62	116–120	80
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	94	122–125	80
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	90	146–147	80
C <sub>6</sub> H <sub>5</sub>	a	55	182–183	80
Adamantyl	CH <sub>3</sub>	80	171 dec	80
(EtO) <sub>2</sub> PO(CH <sub>2</sub> ) <sub>2</sub> -	CH <sub>3</sub>	100		80
3-Pyridyl	CH <sub>3</sub>	100	116–118	80
	CH <sub>3</sub>	100	212 dec	80
-(CH <sub>2</sub> ) <sub>4</sub> - <sup>b</sup>	CH <sub>3</sub>	100	191–192	80
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub>	CH <sub>3</sub>	100	72–73	42
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CONHCH <sub>2</sub>	CH <sub>3</sub>	100		77
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CON(C-C <sub>6</sub> H <sub>11</sub> )CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	99	Oil	77
CH <sub>2</sub> =C(CH <sub>3</sub> )CONHCH <sub>2</sub>	CH <sub>3</sub>	54	108.5–111	77
CH <sub>2</sub> =C(CH <sub>3</sub> )CON(C-C <sub>6</sub> H <sub>11</sub> )CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	87	116–118	77
CH <sub>2</sub> =CHCON(C-C <sub>6</sub> H <sub>11</sub> )CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	100	Oil	77
CH <sub>2</sub> =C(CH <sub>3</sub> )CON(C <sub>4</sub> H <sub>9</sub> )CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	100	Oil	77
CH <sub>2</sub> =C(CH <sub>3</sub> )CON(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	100	Oil	77
CH <sub>2</sub> =C(CH <sub>3</sub> )CON(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub>	CH <sub>3</sub>	100	130–131	77
CH <sub>2</sub> =CHCONHCH <sub>2</sub>	CH <sub>3</sub>	100	136–138	77
C <sub>6</sub> H <sub>5</sub> NHCH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	85	103.5–107	78
3-ClC <sub>6</sub> H <sub>4</sub> NHCH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	87	100.5–101.5	78
2,6-Diamino-5-chloropyrazinyl	CH <sub>3</sub>	79	173–175 dec	82

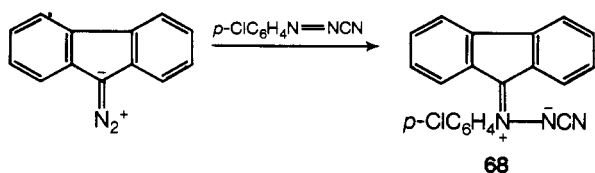
<sup>a</sup> Cyclohexene oxide was used as starting material. <sup>b</sup> A bis(aminimide) was formed.

with sodium hydride.<sup>97a</sup> The use of chloroacetylhydrazones of aromatic ketones (**66**) in this reaction gave the 1-(diarylmethylene)-3-oxo-1,2-diazetidinium inner salts (**67**).<sup>97b,98</sup>

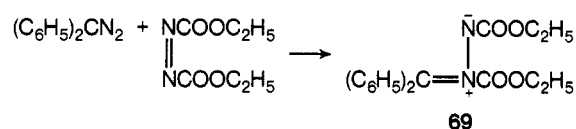


- a**, Ar = Ar' = C<sub>6</sub>H<sub>5</sub>; R = H  
**b**, Ar = C<sub>6</sub>H<sub>5</sub>; Ar' = C<sub>6</sub>H<sub>4</sub>Br-*p*; R = H  
**c**, Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>; Ar' = C<sub>6</sub>H<sub>5</sub>; R = H  
**d**, Ar = Ar' = 2,2'-biphenyl; R = H  
**e**, Ar = Ar' = R = C<sub>6</sub>H<sub>5</sub>

Open-chain derivatives of this system (**68**, **69**) have

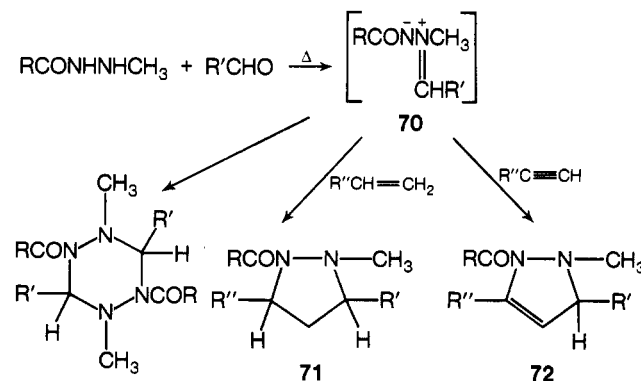


(97) (a) R. B. Greenwald and E. C. Taylor, *J. Amer. Chem. Soc.*, **90**, 5273 (1968); (b) N. F. Haley, Ph.D. Thesis, Princeton University, 1971.  
(98) R. B. Greenwald and E. C. Taylor, *J. Amer. Chem. Soc.*, **90**, 5272 (1968).



been obtained by the reaction of *anti-p*-chlorobenzenediazocarbonyl with diazofluorene<sup>99</sup> and of diphenyldiazomethane with ethyl azodicarboxylate.<sup>100</sup>

Structure **70** has been postulated as an intermediate in the formation of pyrazolidines (**71**) and pyrazoline (**72**) in



(99) R. Huisgen, R. Fleischmann, and A. Eckell, *Tetrahedron Lett.*, **No. 12**, 1 (1960).  
(100) G. F. Bettinetti and L. Capretti, *Gazz. Chim. Ital.*, **95**, 33 (1965).

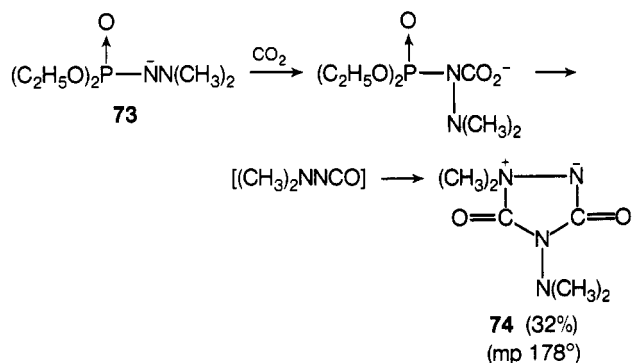
**TABLE XIII. 1-Substituted Methylene-3-oxopyrazolinium Hydroxide Inner Salts (63)**

R	R'	Yield, %	Mp, °C	Ref
CH <sub>3</sub>	CH <sub>3</sub>	90	156–160	94
H	C <sub>6</sub> H <sub>5</sub>	82	205–208	94
	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> <sup>a</sup>	94	155–160	94
	CD <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CD <sub>2</sub> <sup>a</sup>	79	155–160	94
H	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	83	214–217	94
H	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	80	187–189	94
H	2-Furyl	72	213–216	94
H	5-Nitro-2-furyl		230 dec	93
H	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	89	244–246	94
H	<i>p</i> -(ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	80	152–156	94
CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> COOH	68–88		96
CH <sub>3</sub>	CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>			96

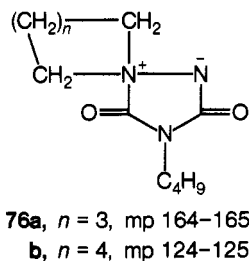
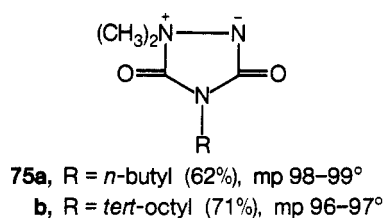
<sup>a</sup> Cyclohexylidene.

the reaction of 1-methyl-2-acylhydrazines, aldehydes, and olefins or acetylenes.<sup>101,102</sup>

Reactions aimed at the synthesis of *N*-dimethylaminoisocyanate have led to its dimer which has an aminimide structure **74**.<sup>103</sup> Sodium dimethyl *N*-dimethylaminophosphoramidate (**73**) when treated with carbon dioxide also gave **74**.



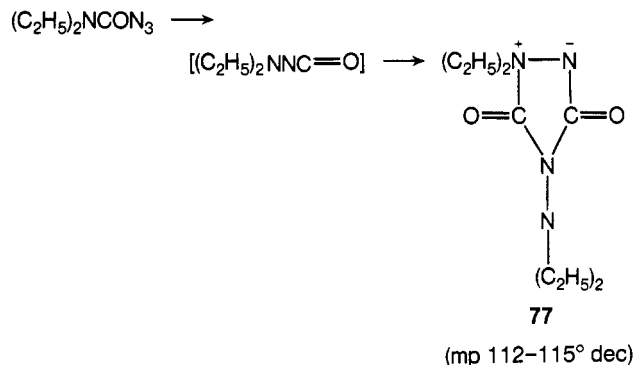
The same reaction in the presence of butyl isocyanate or *tert*-octyl isocyanate gave the mixed dimers **75**. This reaction was extended to spiro derivatives **76** by the use



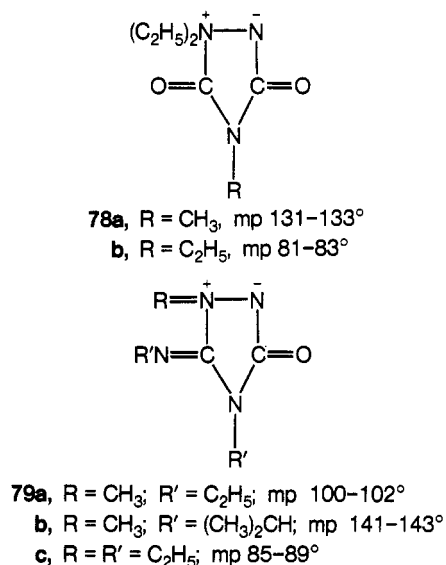
of the sodium dimethyl phosphoramidate derivative of piperidine and hexahydroazepine and butyl isocyanate.<sup>104</sup>

(101) W. Oppolzer, *Tetrahedron Lett.*, 2199 (1970).(102) W. Oppolzer, *Tetrahedron Lett.*, 3091 (1970).(103) W. S. Wadsworth and W. D. Emmons, *J. Org. Chem.*, **32**, 1279 (1967).

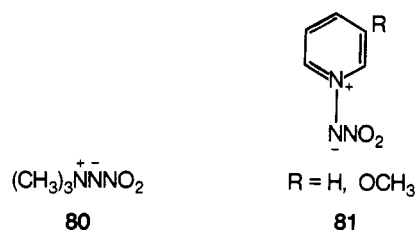
A similar type of product (**77**) was obtained by the photolysis of diethylcarbamoyl azide in aprotic solvents.



In the presence of methyl and ethyl isocyanate and diethyl and diisopropylcarbodiimides, the mixed dimers **78** and **79** are formed, respectively.<sup>105</sup>

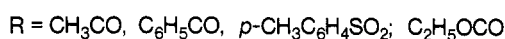
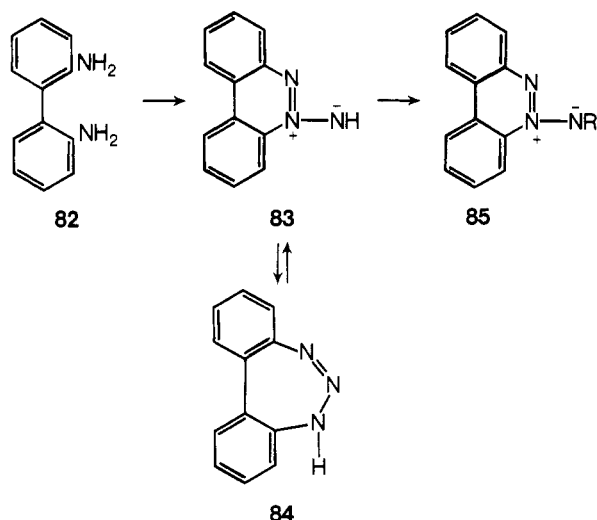


Trimethylamine nitroimide (**80**) has been prepared by treating 1,1,1-trimethylhydrazinium nitrate with acetic anhydride.<sup>106</sup> The corresponding pyridine derivatives (**81**) has been made by the nitration in acetic anhydride of either 1-aminopyridinium nitrate, pyridine-1-benzenesulfonimide or pyridine-1-benzimide.<sup>35</sup>



Aminimides in the benzocinnoline series (**85**) have been prepared by a novel nitrosation of 2,2'-diaminobiphenyl (**82**). Treatment of the latter (**82**) with pentyl nitrite or *N*-nitrosodiphenylamine in benzene gave benzocinnolin-6-imine (**83**) which was converted into various aminimides (**85**).<sup>107</sup> A triazepine (**84**) was considered to be an intermediate in this reaction.

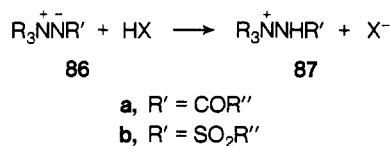
(104) W. S. Wadsworth and W. Bruxvoort, *Chem. Commun.*, 542 (1968).(105) W. Lwowski, R. A. deMauriac, R. A. Murray, and L. Lunow, *Tetrahedron Lett.*, 425 (1971).(106) J. Epsztajn and A. R. Katritzky, *Tetrahedron Lett.*, 4739 (1969).(107) S. F. Gait, C. W. Rees, and R. C. Storr, *Chem. Commun.*, 1545 (1971).



### III. Chemical Properties

#### A. Basicity

Aminimides (**86**) are acid-accepting compounds and react with inorganic and organic acids at room temperature to form hydrazinium salts (**87**). 1-Ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetamide, for example, formed a crystalline salt with L-dibenzoyltartaric acid which could be separated into diastereoisomeric salts. Treatment with alkali gave the optically active aminimides.<sup>52</sup> The  $pK_a$ 's of various aminimides have been determined and are listed in Table XIV.



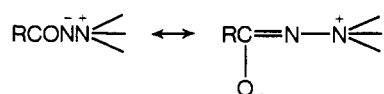
Stronger treatment with acid such as refluxing for 2 hr with hydrochloric acid converted pyridine-1-*p*-acetaminobenzenesulfonimide into 1-aminopyridinium chloride, sulfanilic acid, and acetic acid<sup>13</sup> and 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetamide into 1,1-dimethyl-1-*p*-nitrobenzylhydrazinium chloride.<sup>39</sup>

Aminimides **86** are stable to alkali; trimethylamine-benzimide (**86**, R = CH<sub>3</sub>; R' = COC<sub>6</sub>H<sub>5</sub>) was not affected by boiling with 6 *N* sodium hydroxide for 24 hr.<sup>109</sup> A similar behavior was observed with pyridine-1-*p*-acetaminobenzenesulfonimide; refluxing with 20% sodium hydroxide for 3 hr gave pyridine-1-*p*-aminobenzenesulfonimide.<sup>13</sup>

Solutions of trimethylamine-acylimides in water are reported to be neutral.<sup>64</sup> Trimethylamine-*p*-toluenesulfonimide, which forms a stable hydrate, gave a solution with a pH of 7.9<sup>31</sup> at a concentration of  $4.19 \times 10^{-3}$  *M* in water.

#### B. Alkylation

Since acylaminides have a resonance stabilized structure

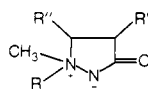


(108) T. Okamoto, M. Hirobe, Y. Tamai, and E. Yabe, *Chem. Pharm. Bull.*, **14**, 506 (1966).

(109) R. F. Smith and P. C. Briggs, *Chem. Commun.*, 120 (1965).

TABLE XIV. Values of  $pK_a$  of Aminimides

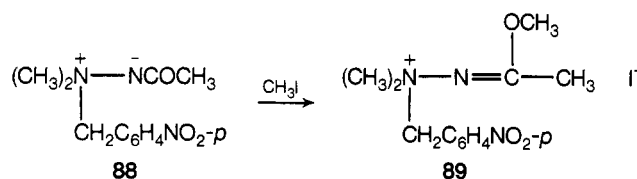
Aminimide	$pK_a$	Ref
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}^+\text{N}^-(\text{CH}_3)_3$	4.2	31
$\text{C}_{12}\text{H}_{25}\text{SO}_2\text{N}^+\text{N}^-(\text{CH}_3)_3$	3.1	33
$\text{C}_{11}\text{H}_{23}\text{CON}^+\text{N}^-(\text{CH}_3)_3$	5.3	33
$\text{CH}_3\text{CON}^+\text{N}^-\text{C}_5\text{H}_5^a$	3.6	108
$\text{C}_6\text{H}_5\text{CON}^+\text{N}^-\text{C}_5\text{H}_5^a$	3.2	35
$\text{NO}_2\text{N}^+\text{N}^-\text{C}_5\text{H}_5^a$	-4.6	35



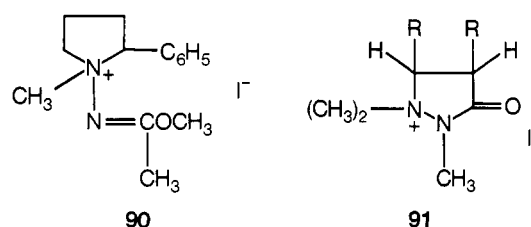
R = R' = CH <sub>3</sub> ; R'' = H	3.0	86
R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ; R' = CH <sub>3</sub> ; R'' = H	2.8	86
R = R' = CH <sub>3</sub> ; R'' = H	2.8	86

<sup>a</sup> C<sub>5</sub>H<sub>5</sub>N = pyridyl.

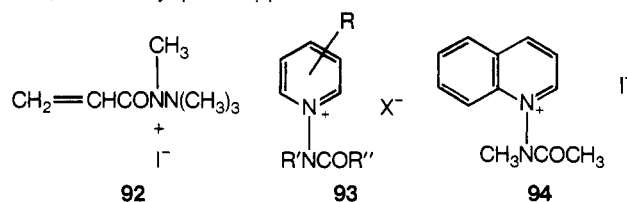
alkylation can proceed on either the oxygen or nitrogen atoms. The actual course of the reaction apparently depends on the groups involved. 1,1-Dimethyl-1-*p*-nitrobenzylamine-2-acetamide (**88**) when treated with methyl iodide gave 1,1-dimethyl-1-*p*-nitrobenzyl-2- $\alpha$ -methoxyethylidenehydrazonium iodide (**89**) and a small amount of *p*-nitrobenzyl iodide.<sup>39</sup> Proof of structure **89** was its hydrolysis with acid to 1,1-dimethyl-1-*p*-nitrobenzylhydrazinium iodide.



1-Methyl-1-acetyl-imide-2-phenylpyrrolidine behaved in a similar fashion and gave the *O*-methyl derivative (**90**).<sup>57</sup> The structure assignments was made on the basis of the ir absorption for the C=N group at 1633 cm<sup>-1</sup>.



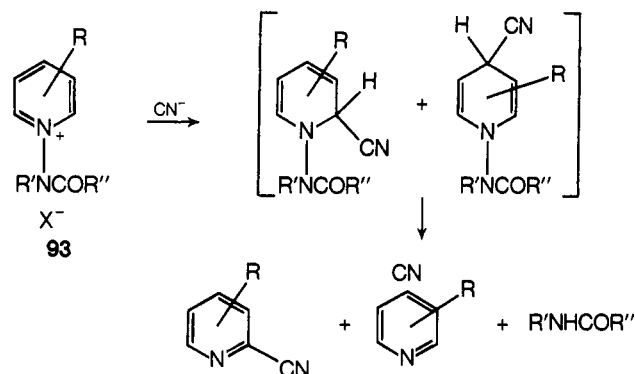
Alkylation of 1,1-dimethyl-3-oxopyrazoline hydroxide inner salts, trimethylamine-acrylimide, pyridine-1-acylimides, and quinoline-1-acetamide occurred on the nitrogen and gave compounds **91-94**. Assignments of structures for **91**<sup>84</sup> and **92**<sup>47</sup> were made on the basis of an infrared absorption at 1670 and 1700 cm<sup>-1</sup>, respectively. The nmr spectrum of **91** was in agreement with this formulation; the methyl peak appeared at  $\delta$  3.1.<sup>90</sup>



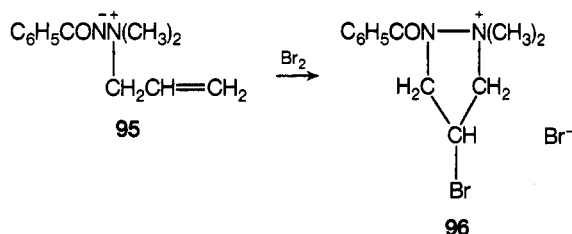
Isoquinoline-2-carbathoxyimide and isoquinoline-2-thiocarbamoylimide are reported to undergo alkylation on the nitrogen and sulfur, respectively.<sup>62</sup>

Alkylation of pyridine-1-acetamides<sup>67,68</sup> was carried out with methyl iodide, allyl bromide, and ethyl bromoacetate

and that of pyridine-1-benzimide with dimethyl sulfate and gave **93**. Proof for this structure was its reaction with potassium cyanide to give 2-cyano- and 4-cyanopyridines and the corresponding substituted amide. The quinoline analog (**94**) behaved in a similar fashion<sup>68</sup> but pyridine-1-acetimide was not affected by cyanide ion.<sup>108</sup>



An intramolecular alkylation is reported to occur when 1,1-dimethyl-1-allylamine-benzimide (**95**) was treated with bromine.<sup>53</sup>



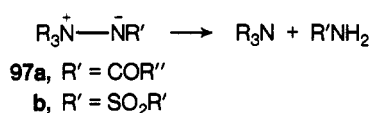
Trimethylamine-*p*-toluenesulfonimide when treated with benzyl chloride gave a compound which had the composition of 1,1,1-trimethyl-2-benzyl-2-*p*-toluenesulfonylhydrazinium chloride. This structure was not demonstrated conclusively.<sup>31</sup>

### C. Oxidation

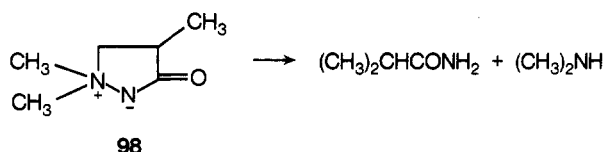
The only reference<sup>31</sup> to the oxidation reports that trimethylamine-*p*-toluenesulfonylimide and 30% hydrogen peroxide gave *p*-toluenesulfonamide; no trimethylamine oxide was isolated.

### D. Reduction

Aminimides **97** are cleaved by zinc and acetic acid<sup>37</sup> and by Raney nickel<sup>37</sup> into the amide and tertiary amine.

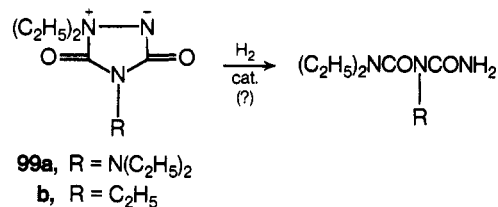


The first reagent has been used successfully with trimethylamine-*p*-toluenesulfonylimide.<sup>31</sup> Raney nickel has been used to cleave trimethylamine-benzimide, trimethylamine-3-pyridinecarboximide,<sup>37</sup> and 1,1,4-trimethyl-3-oxopyrazoline hydroxide inner salt (**98**).<sup>84</sup>

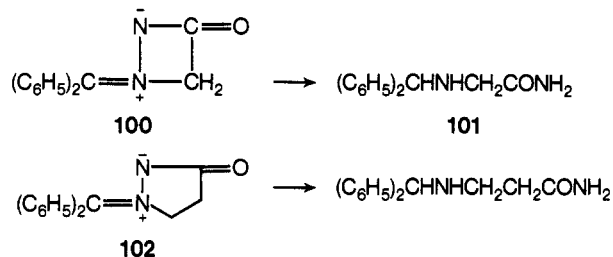


Reductive cleavage has been also reported for 1,1-dimethyl-1-phenylamine-2-phenylpropionimide to dimethylaniline<sup>73</sup> and the dimer of diethyl aminoisocyanate (**99a**)

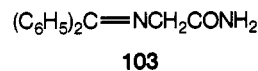
and the mixed dimer with ethyl isocyanate (**99b**) to carbamoylureas.<sup>105</sup>



A similar reductive cleavage with Raney nickel as catalyst was observed with 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium hydroxide inner salt (**100**) and 1-(diphenylmethylene)-3-oxopyrazolinium hydroxide inner salt (**102**).



Reduction of **100** using hydrogen and deactivated Raney nickel led to selective cleavage of the N-N bond and formation of the imine **103**, which is apparently the intermediate in the formation of **101** when a more active catalyst is employed.<sup>97a</sup> Sodium borohydride reduced the -C=N- bond in **100** and **102**.<sup>97</sup>



The reduction of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide with tin and hydrochloric acid was complex; only 1,1-dimethylhydrazine was isolated.<sup>39</sup>

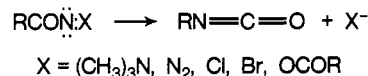
### E. Thermolysis

#### 1. Acylaminimides

Acylaminimides are stable compounds but when heated at or above their melting points undergo the following three types of reactions: (a) nitrogen-nitrogen bond cleavage, (b) rearrangement, and (c) elimination. The actual course of the reaction will depend upon the groups present.

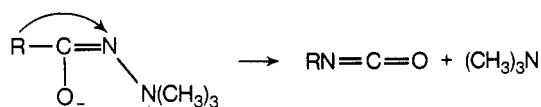
##### a. Nitrogen-Nitrogen Bond Cleavage

Aminimides are structurally similar to the intermediates postulated in the Curtius, Hoffman, Schmidt, and Lossen rearrangement and on heating form isocyanates and trimethylamine.

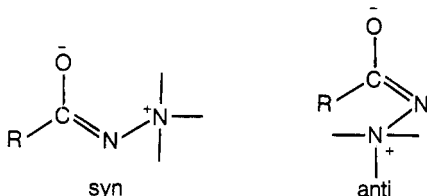


The isocyanate is formed by a concerted mechanism similar to the Curtius rearrangement and does not involve the intermediate formation of a nitrene. Efforts to trap an intermediate nitrene by heating trimethylamine-dodecanimide in dimethyl sulfoxide or in decalin in the presence of triphenylphosphine gave only di-*n*-undecylurea; this product is formed by the action of moisture on the isocyanate.<sup>110</sup>

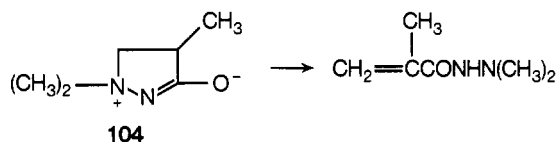
(110) P. Robson and P. R. H. Speakman, *J. Chem. Soc. B*, 463 (1968).



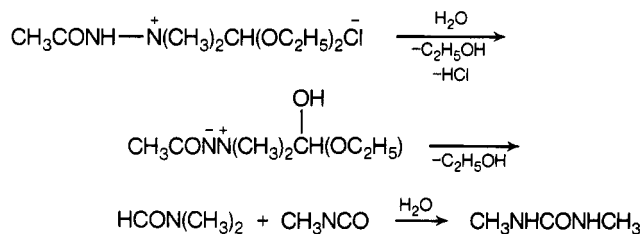
Evidence<sup>51</sup> based on the ratio of Curtius product to the Wawzonek rearrangement product shown in Table XV favored the syn conformer as the precursor of the Curtius product. The greater the steric requirements of R, the greater the population of the syn conformer.<sup>51</sup> Attempts to determine the ratio of syn and anti conformers for trimethylamine-acetamide by spin-echo techniques using low-temperature nmr techniques were not successful.<sup>43, 111</sup>



Further support for the steric requirement is the behavior of 1,1,4-trimethyl-3-oxopyrazolinium hydroxide inner salt (**104**) on thermolysis.<sup>86</sup> This compound which has fixed anti conformation does not form an isocyanate.



The thermolysis is carried out either at atmospheric pressure, at reduced pressure, or in a high-boiling solvent. One reported exception is the aminimide prepared *in situ* by the aqueous reaction of base on the addition product of *N*-chloroacetamide and dimethylformamide diethyl acetal; this product at room temperature gave *unsym*-dimethylurea.<sup>112</sup> The yields of isocyanates prepared by thermolysis are given in Table XVI.



This method is suitable for the preparation of aromatic isocyanates only if a 1,1-dimethyl-1-phenylamine-arylimide is used.<sup>50</sup> Trimethylamine-benzimide on pyrolysis formed phenyl isocyanate trimer (triphenyl isocyanurate),<sup>57, 109, 113</sup> Other products obtained in smaller amounts were benzanilide, 1,3-diphenylurea, carbon dioxide, and 2-phenylbenzimidazole (**105**)<sup>44</sup> and were considered to be formed from the reaction of phenyl isocyanate with the aminimide as shown (Scheme II). The *sym*-diphenylurea may result from the reaction of the isocyanate with moisture.

Proof for the involvement of phenyl isocyanate was the formation of 2-phenyl-1*H*-naphth[1,2-*d*]imidazole (**106**) in the thermolysis of trimethylamine-benzimide in the presence of  $\alpha$ -naphthyl isocyanate.

(111) L. Michael, Ph.D. Thesis, University of Cincinnati, 1969.

(112) H. Brederick, G. Simchen, and H. Porkert, *Chem. Ber.*, **103**, 257 (1970).

(113) H. S. Gibson and A. W. Murray, *J. Chem. Soc.*, 880 (1965).

TABLE XV. Thermolysis of  $\text{RCO}\ddot{\text{N}}\text{N}^+\text{CH}_2\text{C}_6\text{H}_5(\text{CH}_3)_2$  in Nitrobenzene

R	Curtius product, %	Wawzonek product, %
CH <sub>3</sub>	69	31
(CH <sub>3</sub> ) <sub>2</sub> CH	99	1
(CH <sub>3</sub> ) <sub>3</sub> C	99.8	0.2

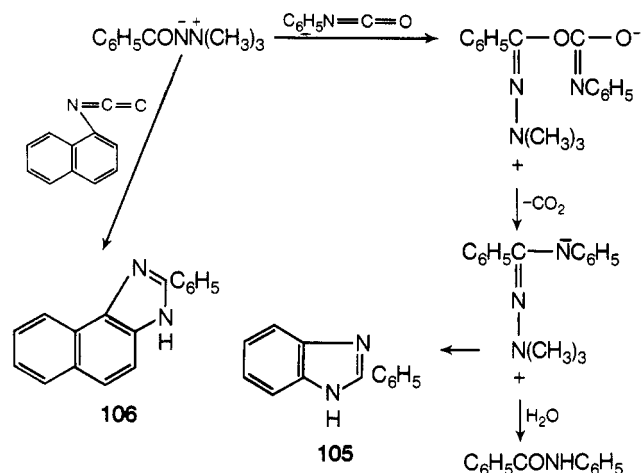
TABLE XVI. Yields of Isocyanates from Aminimides

R	Yield, % RNCO	Ref
(CH <sub>3</sub> ) <sub>2</sub> CHCOC(CH <sub>3</sub> ) <sub>2</sub>	75	48
-(CH <sub>2</sub> ) <sub>8</sub> - <sup>a</sup>	80	48
CH <sub>2</sub> =C(CH <sub>3</sub> )	86	45
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub>	71	42
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CHCH <sub>2</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub>	50	42
Phenylheptadecyl (commercial)	20-30	42
Dimer acid (Emery Empol 1010)	75	42
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CON(C-C <sub>6</sub> H <sub>11</sub> )CH <sub>2</sub> CH <sub>2</sub>	100	77

R	Amine	RNCO	Ref
CH <sub>3</sub>	Phenyl-1-methylpyrrolidene	38	57
CH <sub>3</sub>	2-Phenyl-1-methylpiperidine	24	58
C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>5</sub>	94	56
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub>	(CH <sub>3</sub> ) <sub>2</sub> NC(OCOCH <sub>3</sub> )H(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	39	80

<sup>a</sup> Bis.

#### SCHEME II



1-Methylpiperidine-1-benzimide in this reaction gave the trimer, methylpiperidine, and 2-phenylbenzimidazole (**105**); trimethylamine-3-methoxybenzimidazole when decomposed in  $\alpha$ -methyl-naphthalene gave the trimer and urea.<sup>44</sup>

Decomposition of trimethylamine-benzimide in the presence of aniline<sup>109</sup> or *p*-bromoaniline<sup>113</sup> converted the phenyl isocyanate generated *in situ* into the diarylurea before it was trimerized by the trimethylamine.

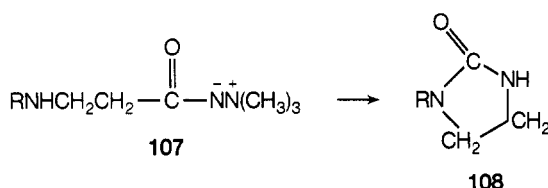
Trapping of the isocyanate can also be accomplished with alcohols and forms urethanes. Pyrolysis of 1,1-dimethyl-1-(2-hydroxyoctyl)amine-laurimide, for example, gave diundecylurea and an oil which had an infrared spectrum similar to the urethane from undecyl isocyanate and 1,1-dimethyl-1-(2-hydroxyoctyl)amine.<sup>80</sup>

**TABLE XVII. Thermolysis of Aminimides to 1-Substituted-2-imidazolidinones (108)**

R	% yield of imidazolidinone	Mp, °C	Bp, °C (mm)
<i>n</i> -Butyl	88	36–39	102 (0.3)
Allyl	82	56.5–58	95 (0.25)
Cyclohexyl	82	167–167.5	
Phenyl	90	162–162.5	
Phenyl	80	161–163	
<i>m</i> -Chlorophenyl	64	126–126.5	
<i>m</i> -Chlorophenyl	90	126–127	
<i>m</i> -Tolyl	85	142.5–143	
Furfuryl	61	97.5	131–135 (0.3)
3-Picolyl	31	92–93.5	
2-Pyridinoethyl	35	93–94.5	

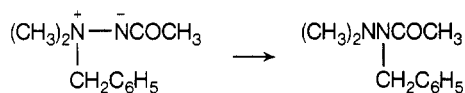
Urethanes were formed by treating hydroxyl-terminated esters with bis(trimethylamine)azelaamide and isophthalamide,<sup>48</sup> and poly(dimethyl- $\beta$ -hydroxypropylamine-methacrylimide-styrene) copolymers with either bis(2-hydroxyethyl) azelate, bis(2-hydroxyethyl) dimerate, or Epon 812 (Shell Chemical Co. trademark).<sup>114</sup> Thermolysis of polymers from 1,1-dimethyl-1-(2,3-dihydroxypropyl)-amine-methacrylimide,<sup>81</sup> and trimethylamine-*N*-laurolyglycinimide<sup>77</sup> gave polymeric carbamates and *N*-lauroly-substituted poly(methyleneurea), respectively.

Pyrolysis of aminimides **107** from  $\beta$ -substituted aminopropionic acid gave 1-substituted-2-imidazolidinones **108**.<sup>78</sup> The imidazolidinones prepared by this method are shown in Table XVII.



### b. Rearrangement

Aminimides containing either a benzyl,<sup>40</sup> allyl,<sup>53</sup> or propargyl<sup>115</sup> group on the cationic nitrogen, when heated, undergo a rearrangement with migration of these groups to the anionic nitrogen.



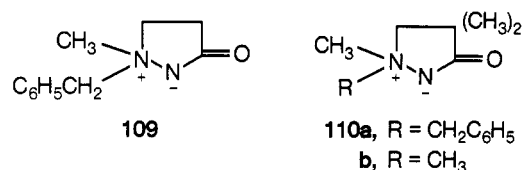
This rearrangement which was first observed with 1,1-dimethyl-1-benzylamine-acetamide and 1,1-dimethyl-1-*p*-nitrobenzylamine-acetamide<sup>40</sup> is known as the "Wawzonek rearrangement." This migration of groups, which also occurs with cyclic aminimides,<sup>86</sup> has been shown to proceed by a homolytic cleavage followed by a recombination of the radicals similar to the Stevens rearrangement of nitrogen ylides. Nmr studies of the rearrangement of 1,1-dimethyl-1-*p*-nitrobenzylamine-acetamide<sup>116</sup> in nitrobenzene and of 1-methyl-1-benzyl-3-oxopyrazolinium hydroxide inner salt (**109**)<sup>117</sup> found a chemically induced dynamic nuclear polarization (CIDNP) emission signal related to the benzyl resonance. A similar observation has

(114) B. M. Culbertson and N. A. Randen, *J. Appl. Polym. Sci.*, **15**, 2609 (1971).

(115) Z. H. Gegelyan, K. P. Kiramidzhyan, M. G. Indzhikyan, and A. Babayan, *Arm. Khim. Zh.*, **23**, 1010 (1970).

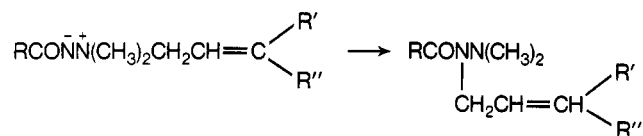
(116) R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226 (1969).

(117) D. G. Morris, *Ind. Chim. Belge*, **36**, 1060 (1971).

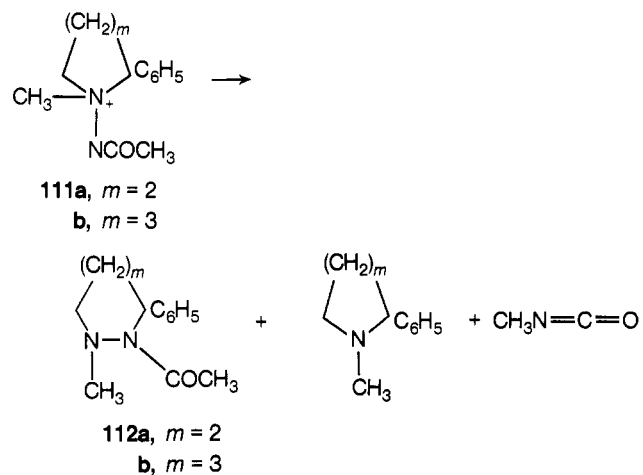


been reported for 1,1-dimethyl-1-cinnamylamine-acetamide.<sup>54</sup>

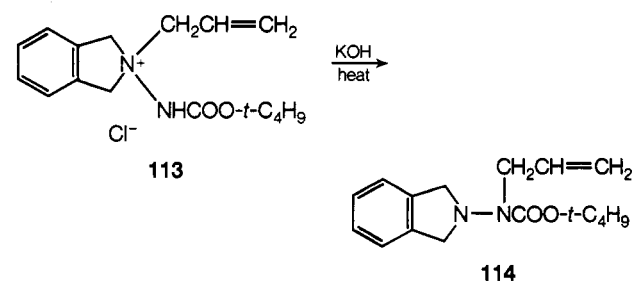
Chemical evidence for the free-radical mechanism is the rearrangement of the crotyl, cinnamyl, and  $\gamma,\gamma$ -dimethylallyl groups without isomerization,<sup>54</sup> and the trapping of the benzyl group in the rearrangement of 1,1-dimethyl-1-benzylamine-acetamide and 1,4,4-trimethyl-1-benzyl-3-oxopyrazolinium hydroxide inner salt (**110a**) with benzylthiol and bromotrichloromethane; toluene and benzyl bromide were formed, respectively.<sup>118</sup> This free radical rearrangement is apparently accompanied by a small amount of concerted rearrangement in the pyrolysis of the crotyl derivative.<sup>115</sup> The Wawzonek rearrangement can be accompanied by the formation of the isocyanate, and, as mentioned earlier, would be favored by the anti conformer of the aminimide.<sup>51</sup>



The benzyl group if present in a ring (**111**) will migrate with a resulting ring expansion. 1-Methyl-2-phenylpyrrolidine-1-acetamide (**111a**)<sup>57</sup> and 1-methyl-2-phenylpiperidine-1-acetamide (**111b**)<sup>58</sup> gave 1-methyl-2-acetyl-3-phenylhexahydropyridazine (**112a**) and 1-methyl-2-acetyl-3-phenylhexahydro-1,2-diazepine (**113b**); methyl isocyanate and the corresponding tertiary amine were also formed.



If an allyl group is present on the cationic nitrogen of a heterocyclic ring (**113**), it migrates in preference to the benzyl group.<sup>119</sup>

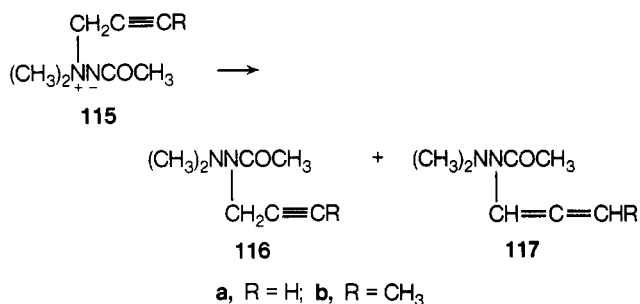


(118) H. P. Benecke and J. H. Wikel, *Tetrahedron Lett.*, 3479 (1971).

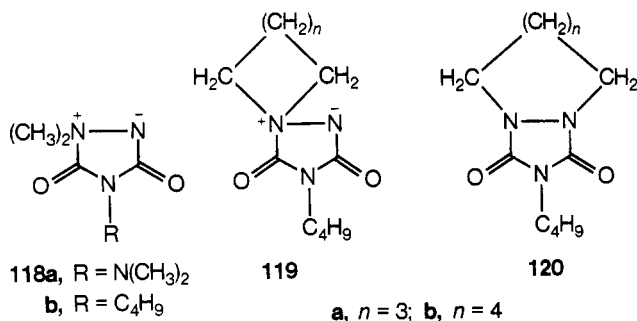
(119) B. Zeeh and K. H. Konig, *Synthesis*, 45 (1972).



Pyrolysis of propargyldimethylamine-acetimide (**115a**) gave a mixture of the propargyl (**116a**) and the allene derivatives (**117a**).<sup>115</sup> The methyl propargyl derivative (**115**) is reported to give the allene derivative (**117**, R = CH<sub>3</sub>).



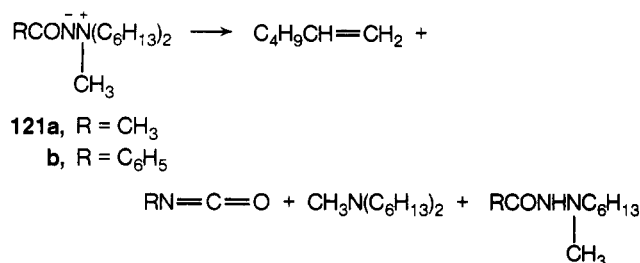
Migration of a methyl group has been observed with dimers from dimethylaminoisocyanate (**118**)<sup>103</sup> and with 1,1,4,4-tetramethyl-3-oxopyrazolidinium hydroxide inner salt (**110b**).<sup>43</sup> The spiro derivative (**119**) underwent ring expansion when  $n = 4$  to **120**.<sup>104</sup> The lower homolog (**119**,  $n = 3$ ) was stable to thermolysis.



### c. Elimination

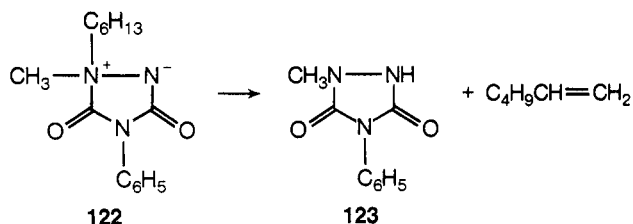
Aminimides substituted with a group with two or more carbons and a  $\beta$  hydrogen on the cationic nitrogen upon thermolysis undergo a cis elimination reaction similar to amine oxides. 1,1-Dimethyl-1-(2-phenylpropyl)amine-acetimide, for example, gave a 79% yield of 2-phenylpropene, and 1,1-dimethyl-1-octylamine-acetimide gave an 82% yield of cyclooctene which consisted of 96.5% cis and 3.5% trans isomers.<sup>55</sup>

1,1-Dihexyl-1-methylamine-2-acylimides (**121**)<sup>56</sup> on thermolysis underwent an elimination reaction together with isocyanate formation. The acetyl derivative (**121a**) gave 1-hexene, methyl isocyanate, 1-hexyl-1-methyl-2-acetylhydrazine, and dihexylmethylamine. Based on the ratio of the last two compounds, the elimination reaction occurred to the extent of 64.5%.

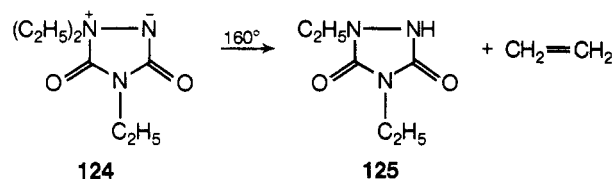


The benzoyl derivative (**121b**) on thermolysis gave 1-hexene, dihexylmethylamine, benzanilide, *sym*-diphenylurea, 2-phenylbenzimidazole, and 1-phenyl-3-methylurazole. The formation of the last four compounds can be explained by secondary reactions between phenyl isocyanate and the aminimide **121b** (see ref 44) and 1-hexyl-1-methyl-2-benzoylhydrazine. The last compound and phenyl isocyanate would form benzanilide and methylhex-

ylaminoisocyanate which would be trapped by phenyl isocyanate with the formation of **122**. This compound was



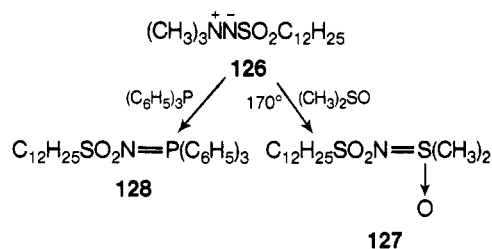
not isolated since it undergoes an elimination reaction with the formation of 1-phenyl-3-methylurazole (**123**). The ratio of elimination to rearrangement for **121b** was 1:4. A similar elimination reaction was reported for the triethyl derivative **124**.<sup>105</sup>



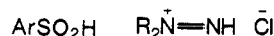
## 2. Sulfonylaminiimides

Sulfonylaminiimides upon thermolysis behave differently from the acyl analogs and form products derived from nitrenes. 1,1,1-Trimethylamine-*p*-toluenesulfonimide upon heating at 185–195° gave trimethylamine, *p*-toluenesulfonamide, ammonia, formaldehyde, and sulfonamide-formaldehyde condensation polymers.<sup>31</sup>

Evidence for a nitrene intermediate was the formation of a sulfoxime (**127**) and triphenylphosphine dodecane-sulfonimide (**128**) in the thermolysis of trimethylamine-dodecanesulfonimide (**126**) in dimethyl sulfoxide, and in tetralin containing triphenylphosphine. Dodecanesulfonamide was formed as a by-product in each case.<sup>110</sup>



Sulfonylaminiimides, with a benzyl or allyl substituents on the cationic nitrogen, exhibit complex behavior when heated. On thermolysis no rearrangement products were isolated. 1,1-Dimethyl-1-benzylamine-*p*-toluenesulfonimide upon heating at 185° gave *p*-tolyl disulfide (4%), benzyl tolyl sulfone (22%), benzaldehyde dimethylhydrazone (5%), *p*-toluenesulfonamide (13%), and benzyldimethylamine (5%). The 3-methyl-2-butenyl derivative gave the sulfide and the corresponding sulfone.<sup>32</sup> The similarity of some of these products to those obtained by the acid hydrolysis of 1,1-dialkyl-2-*p*-tolylsulfonylhydrazine<sup>120</sup> suggest the intermediacy of sulfinic acid and diazenium ions in this reaction.

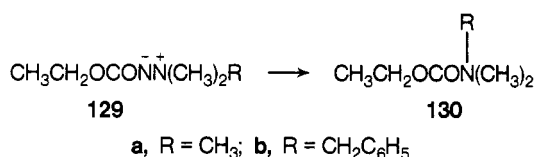


## 3. Carbethoxyaminimides

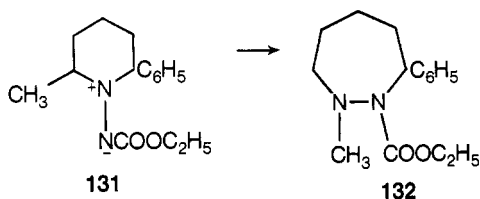
Trimethylamine-carbethoxyimide (**129a**) and benzyldimethylamine-carbethoxyimide (**129b**) upon thermolysis

(120) S. Wawzonek and W. McKillip, *J. Org. Chem.*, **27**, 3946 (1962).

gave exclusively the products (**130**) resulting from a Wawzonek rearrangement.<sup>121</sup> The thermolysis of **129a** is the first reported methyl migration for a noncyclic aminimide, and no evidence was found for nitrene formation.



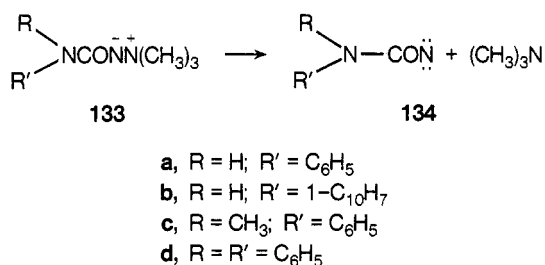
1-Methyl-2-phenylpiperidine-1-carbomethoxyimide (**131**)<sup>58</sup> on thermolysis behaved differently and gave, in addition to the rearranged product **132**, ethyl carbamate which could arise from carbomethoxy nitrene.



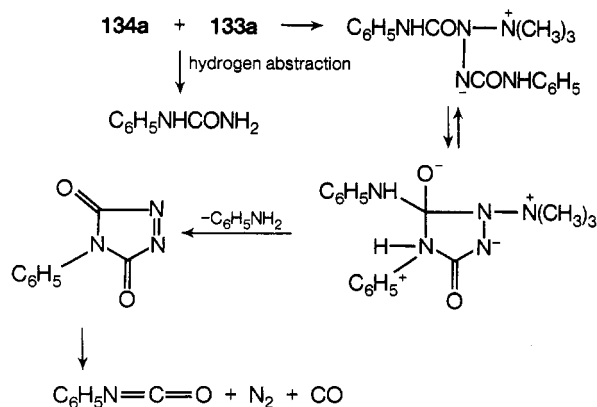
Nitrene formation with insertion is likewise reported for the thermolysis of cinnoline-4-carbomethoxyimide (**85**) in decalin.<sup>107</sup>

#### 4. Carbamoylaminimides

Carbamoylaminimides **133** on thermolysis gave products which parallel those formed from azides.



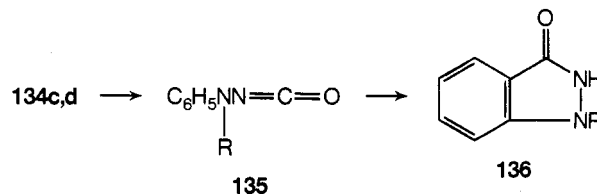
1,1,1-Trimethylamine-2-phenylcarbamoylimide (**133a**) in this reaction gave diphenylurea, phenylurea, 1,1-dimethylhydrazine, 1,1,2-trimethyl-4-phenylsemicarbazide, 1,1-dimethyl-4-phenylsemicarbazide, aniline, trimethylamine, nitrogen, and carbon monoxide.<sup>60,122</sup> A number of these products can be accounted for by the formation of a nitrene (**134a**) and its reaction with the aminimide



**133a.** The intermediacy of azoformanilide, the dimer of the nitrene, was eliminated as a possibility since this compound decomposes at a lower temperature than the

aminimide and forms diphenylurea, formanilide, phenyl isocyanate, carbon monoxide, and nitrogen. The naphthalene derivative **133b** gave similar products.

The behavior of 1,1,1-trimethylamine-2-methyl-2-phenylcarbamoylimide (**133c**) and 1,1,1-trimethylamine-2,2-diphenylcarbamoylimide (**133d**) paralleled that of nonrigid azides.<sup>123</sup> Rearrangement of the intermediate nitrene (**134c,d**) occurred to the *N*-aminoisocyanate **135** which cyclized to the indazolone **136**.



#### 5. Nitroaminimides

Nitroaminimides are thermally stable at 200° for several hours.<sup>106</sup>

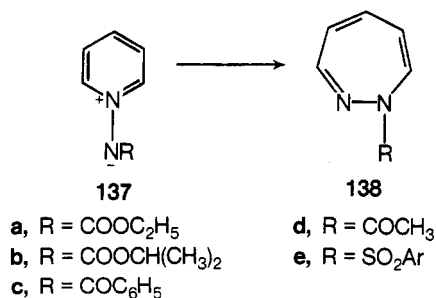
#### F. Photolysis

Photolysis of trialkylamine-acylimides leads either to no reaction or causes mainly N-N bond cleavage with the formation of the amide. Irradiation of trimethylamine-benzimide in methanol gave benzamide (22%), starting material, and oils.<sup>109</sup> The same reaction with trimethylamine-laurimide in dimethyl sulfoxide gave lauramide in poor yields and no nitrene addition product.

Trimethylamine-dodecanesulfonimide<sup>110</sup> was stable to photolysis at 80° in dimethyl sulfoxide in contrast to the corresponding azide.

Trimethylamine-carbomethoxyimide<sup>121</sup> and 1,1,1-trimethylamine-2-phenylcarbamoylimide<sup>122</sup> were not affected by irradiation in methanol; only minute amounts of tarry material were formed.

Aminimides derived from pyridines (**137**) are unique and upon photolysis form diazepines (**138**).<sup>124,125</sup> This reaction does not occur thermally with **137a** at 130°. The benzoyl derivative **137c** in turn at 190–200° gave pyridine and phenyl isocyanate which was trapped with aniline and formed diphenylurea. The isoquinoline derivative in the same reaction gave isoquinoline and benzanilide.<sup>126</sup>



Side reactions are minimal and result in a cleavage of the N-N bond with formation of the pyridine and a nitrene. This reaction was found to increase for the pyridine derivative (**137b**) when triplet photosensitizers such

(121) E. A. Sedor, *Tetrahedron Lett.*, 323 (1971).

(122) R. F. Smith, T. C. Rosenthal, P. T. Hussong, and P. G. Buri, *Tetrahedron Lett.*, 4007 (1970).

(123) W. Lwowski, R. Demauriac, T. W. Mattingly, Jr., and E. Scheifele, *Tetrahedron Lett.*, 3285 (1964).

(124) T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, 432 (1969).

(125) J. Streith and J. M. Cassal, *Angew. Chem., Int. Ed. Engl.*, 7, 129 (1969); *Tetrahedron Lett.*, 4541 (1968).

(126) M. Ikeda, N. Tsujimoto, and Y. Tamura, *Org. Mass Spectrom.*, 5, 61 (1971).

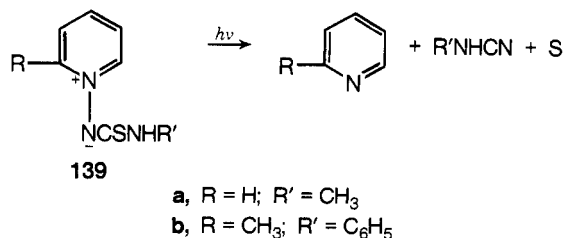
TABLE XVIII. Preparation of Diazepines (138)

Pyridine	R	Solvent	Yield, %	Ref
Pyridine	COOC <sub>2</sub> H <sub>5</sub>	Acetone	95	69
Pyridine	COOC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	93	21
Pyridine	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	93	27
Pyridine	COOCH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	90	28
2-Picoline	COOC <sub>2</sub> H <sub>5</sub>	Acetone	80	69
2-Picoline	COOC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	84	21
4-Picoline	COOC <sub>2</sub> H <sub>5</sub>	Acetone	74	69
4-Picoline	COOC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	98	21
4-Picoline	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	75	28
3-Picoline	COOC <sub>2</sub> H <sub>5</sub>	Acetone	75	69
2,4-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	77	69
2,5-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	Acetone	70	69
3,5-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	Acetone	84	69
3,5-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	47	21
3,4-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	Acetone	80	69
2,6-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	47	69
2,6-Dimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	72	21
2,4,6-Trimethylpyridine	COOC <sub>2</sub> H <sub>5</sub>	Acetone	87	69
4-Dimethylaminopyridine	COOC <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	65	21
2-Cyanopyridine	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	86	27
4-(4'-Chlorobenzoyl)pyridine	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	0 <sup>a</sup>	28
4-Phenylpyridine	COOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	90	28
Pyridine	COCH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	64	21
Pyridine	COCH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	84	22
Pyridine	COCH <sub>3</sub> <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub>	55	127
2-Picoline	COCH <sub>3</sub> <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	127
2-Picoline	COCH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	80	28
2,6-Dimethylpyridine	COCH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	21	28
2,6-Dimethylpyridine	COCH <sub>3</sub> <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	38	127
Pyridine	SO <sub>2</sub> C <sub>7</sub> H <sub>7</sub>	CH <sub>2</sub> Cl <sub>2</sub>	61	21
Pyridine	SO <sub>2</sub> C <sub>7</sub> H <sub>7</sub>	CH <sub>3</sub> CN	16	26
Pyridine	SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>			126

<sup>a</sup> 100% N-N cleavage. <sup>b</sup> 37% CH<sub>3</sub>NCO formed. <sup>c</sup> 33% CH<sub>3</sub>NCO formed. <sup>d</sup> 62% CH<sub>3</sub>NCO formed.

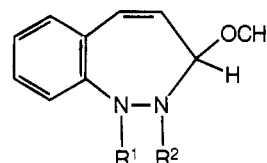
as eosine or 3,4-benzopyrene were added.<sup>28</sup> Pyridine-1-isopropoxycarbonylimide (**137b**) when irradiated in methylene chloride in the presence of oxygen gave none of the side reaction. The same irradiation in acetone in the presence of eosine gave a 58% yield of pyridine. This side reaction with 3,5-dimethylpyridine-1-carbonylimide<sup>21</sup> resulted in the formation of 2-carbonylamino-3,5-dimethylpyridine, and with the pyridine-1-acetimidides (**137d**) gave methyl isocyanate and the pyridine.<sup>127</sup> Examples of diazepines formed by this reaction are given in Table XVIII.

Pyridine-1-(2-methylthiocarbamoyl)imide (**139a**) and 2-methylpyridine-1-(2-phenylcarbonyl)imide (**139b**) gave in this reaction only N-N cleavage with the formation of the pyridine, sulfur, and substituted cyanamide which was only isolated from **139b**.<sup>128</sup>



Aminimides derived from other nitrogen heterocyclic compounds when irradiated form nitrenes and the amine as the main product. Quinoline-1-acetamide in methanol gave quinoline (20%), methyl *N*-methylcarbamate (11%),

2-acetylaminquinoline (19%), and a methanol adduct (6%) which tentatively was assigned a diazepine structure.<sup>129</sup>



2,4-Dimethylthiazole-3-acetamide gave 2,4-dimethylthiazole (14.4%) and methyl *N*-methylcarbamate (6.4%).<sup>129</sup> 1-Benzyl-1,2,4-triazole-4-benzenesulfonamide gave 1-benzyl-1,2,3-triazole (58%) and benzenesulfonamide (14%).<sup>34</sup> Benzocinnoline-6-carbonylimide (**85**) in hexane gave the nitrene with resulting CH insertion.<sup>107</sup> Isoquinoline-2-carbonylimide in water gave *N*-(1-isoquinoline)urea, and the carbonyloxy derivative gave *N*-(1-isoquinoline)urethane.<sup>62</sup> 1,2,4-Triazole-4-acylimides in methanol gave the corresponding triazole and products of the nitrene such as the carbamate, *O*-methylhydroxamic acid, acylamide, methyl ester of the acid, and formaldehyde.<sup>130</sup>

### G. Cycloaddition Reactions

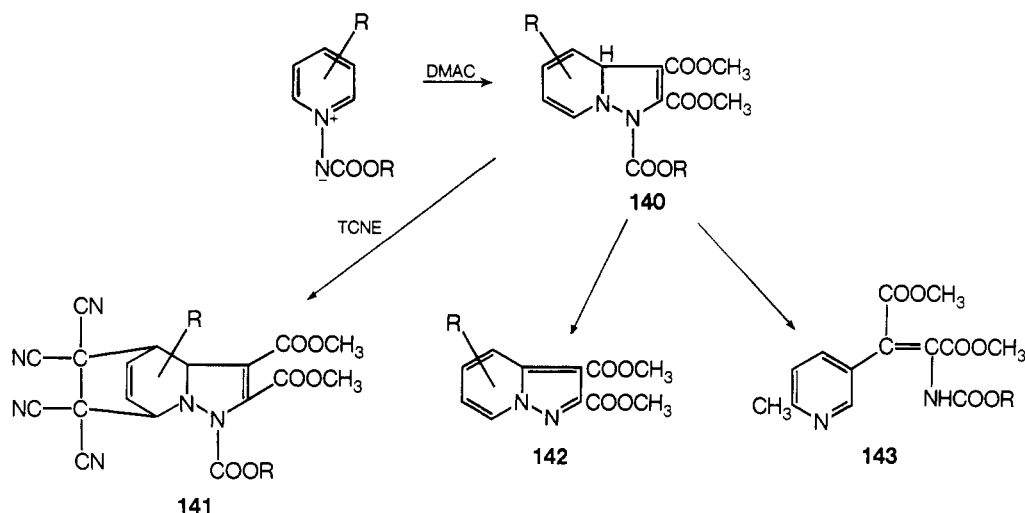
Aminimides derived from pyridine undergo a 1,3-dipolar cycloaddition reaction with dimethyl acetylenedicar-

(127) V. Snieckus, *Chem. Commun.*, 831 (1969).

(128) K. T. Potts and R. Dugas, *Chem. Commun.*, 732 (1970).

(129) T. Shiba, K. Yamane, and H. Kato, *Chem. Commun.*, 1592 (1970).

(130) H. G. O. Becker, D. Beyer, and H. J. Timpe, *Z. Chem.*, 10, 264 (1970).



boxylate<sup>26</sup> and form dihydropyrazolopyridines (**140**) which may either spontaneously aromatize to pyrazolopyridine derivatives (**142**) or rearrange to vinylpyridines (**143**). The same reaction in the presence of TCNE (tetracyanoethylene), which causes dehydrogenation of the dihydro derivative (**140**), gave the pyrazolopyridine (**142**) and the Diels-Alder adduct of the dihydro compound (**141**). The results obtained in both reactions are given in Tables XIX and XX.

**TABLE XIX.** Reaction of Pyridine-1-carbonylimides with Dimethyl Acetylenedicarboxylate

Pyridine	Yield, %		Pyrazolopyridine
	Dihydropyrazolopyridine	Vinylpyridine	
Unsubstituted			1%
3-Methyl			Trace <sup>a</sup>
4-Methyl			27
4-COOC <sub>2</sub> H <sub>5</sub>			28
2-Methyl <sup>b</sup>	12	22	
2-Methyl	11	24	
2,6-Dimethyl <sup>b</sup>	80	3	
2,6-Dimethyl	68	17	
2,4,6-Trimethyl <sup>b</sup>	56	44	
2,3-Dimethyl		43	
2,4-Dimethyl			27
2,5-Dimethyl			5

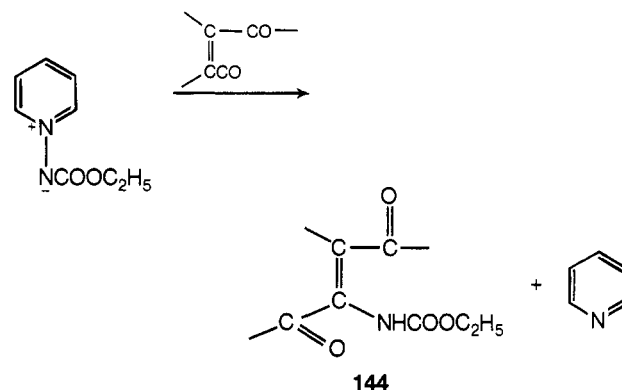
<sup>a</sup> Mixture of isomers. <sup>b</sup> Carbomethoxy derivative.

**TABLE XX.** Reaction of Pyridine-1-carbonylimides with Dimethyl Acetylenedicarboxylate in the Presence of TCNE

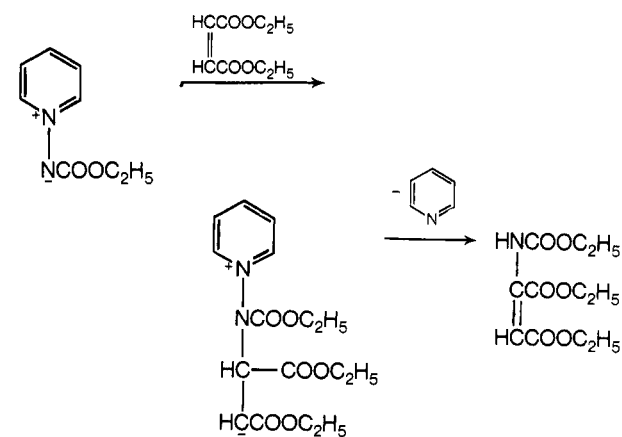
Pyridine	Yield, %	
	Pyrazolopyridine	Diels-Alder adduct
Unsubstituted	5	0
3-Methyl	1 <sup>a</sup>	0
4-Methyl	44	0
4-COOC <sub>2</sub> H <sub>5</sub>	45	0
2-Methyl <sup>b</sup>	40	12
2-Methyl	51	15
2,6-Dimethyl <sup>b</sup>		75
2,6-Dimethyl		62
2,4,6-Trimethyl <sup>b</sup>		67
2,3-Dimethyl	0	
2,4-Dimethyl	46	
2,5-Dimethyl	0	

<sup>a</sup> Mixture of isomers. <sup>b</sup> Carbomethoxy derivative.

The reaction of pyridine-1-carbonylimide with  $\alpha,\beta$ -unsaturated carbonyl compounds proceeds differently from that reported for dimethyl acetylenedicarboxylate. Reaction occurred only in the presence of silicic acid in either refluxing benzene, acetonitrile, or xylene and formed enamines **144** in good yields.<sup>131</sup> Reactions were



carried out with ethyl maleate, ethyl fumarate, maleic anhydride, *N*-phenylmaleimide, benzoquinone,  $\alpha$ -naphthoquinone, and tropone. The products have been rationalized as a nucleophilic reaction of the aminimide with the double bond followed by a hydride shift with elimination of pyridine.

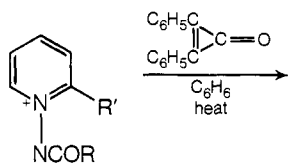


Diphenylcyclopropanone in this reaction gave 1,3-oxazines (**146**).<sup>132</sup> The yield of **146c** was poor. The oxazine

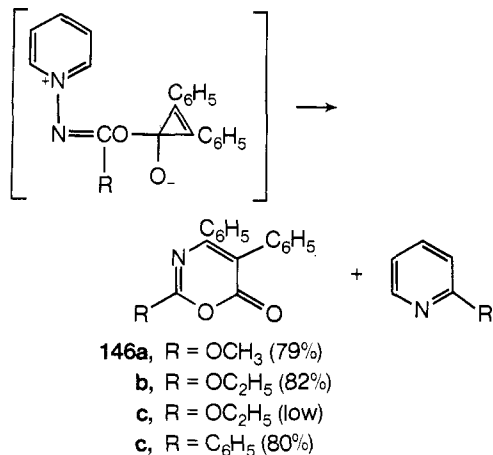
(131) T. Sasaki, K. Kanematsu, and A. Kakehi, *Tetrahedron*, **28**, 1469 (1972).

(132) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2451 (1971).

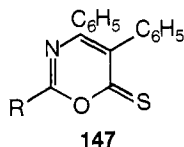
**146** was considered to be formed by a nucleophilic attack of the aminimide on the ketone as shown.



- 145a**, R = OCH<sub>3</sub>; R' = CH<sub>3</sub>  
**b**, R = OC<sub>2</sub>H<sub>5</sub>; R' = CH<sub>3</sub>  
**c**, R = OC<sub>2</sub>H<sub>5</sub>; R' = H  
**d**, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>



Diphenylcyclopropenethione behaves in a similar fashion and gave 2,4,5-trisubstituted-6H-1,3-oxazine-6-thiones (**147**) (see Table XXI).<sup>62</sup>



A cycloaddition reaction between isoquinoline-2-carbonylimide and acrylonitrile has been reported to yield **148**.<sup>62</sup>

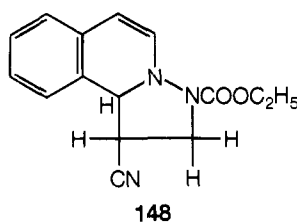


TABLE XXI. Yields of 2,4,5-Trisubstituted-6H-1,3-oxazine-6-thiones (**147**)

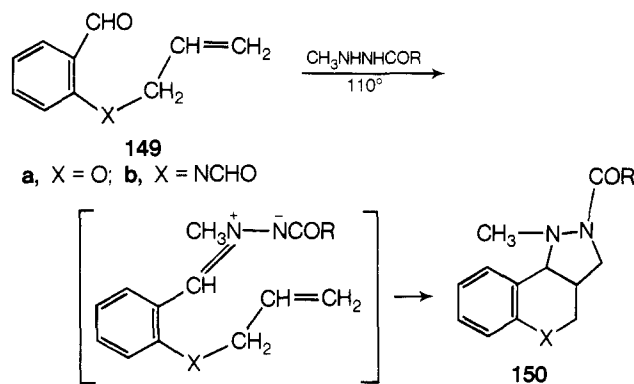
R	Yield, %
C <sub>2</sub> H <sub>5</sub>	63
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	90
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	94
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	83
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	50
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	74
C <sub>6</sub> H <sub>5</sub>	88
C <sub>6</sub> H <sub>5</sub> CH=CH	61
C <sub>4</sub> H <sub>3</sub> SCH=CH <sup>a</sup>	48
C <sub>4</sub> H <sub>3</sub> O <sup>b</sup>	50
C <sub>4</sub> H <sub>3</sub> S <sup>a</sup>	47

<sup>a</sup> C<sub>4</sub>H<sub>3</sub>S = 2-thienyl; <sup>b</sup> C<sub>4</sub>H<sub>3</sub>O = 2-furyl.

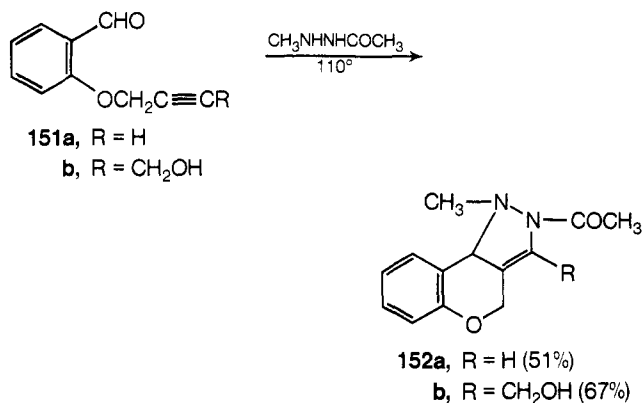
Open-chain aminimides, containing a doubly bonded carbon on the cationic nitrogen, have been generated *in situ* from 1-methyl-2-acylhydrazines and aldehydes and react with olefins and acetylenes to form pyrazolidines (**71**) and pyrazolines (**72**) (see section II.B).<sup>101</sup> Examples of this condensation are given in Table XXII.

The reaction of phenylacetylene, 1-methyl-2-phenylacetylhydrazine, and formaldehyde gave the pyrazoline **72** in a 56% yield.

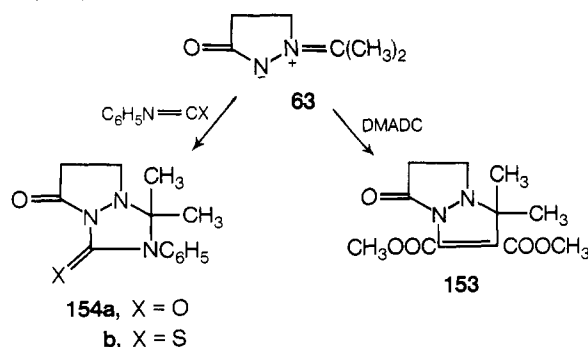
Intramolecular cyclization occurred through a similar intermediate when *O*-allyloxybenzaldehyde (**149a**) or *O*-(allylformylamino)benzaldehyde (**149b**) was treated with a 1-methyl-2-acylhydrazine.<sup>102</sup> Examples of this condensation are given in Table XXIII.



*O*-Propargyloxybenzaldehyde (**151**) and 1-methyl-2-acetylhydrazine in this reaction gave pyrazolines **152**.



1-Isopropylidene-3-oxopyrazolidine hydroxide inner salt (**63**), which is a stable aminimide, behaved in a similar fashion with dimethyl acetylenedicarboxylate, phenyl isocyanate, and phenyl isothiocyanate and gave a dihydropyrazolopyrazole (**153**) and perhydropyrazolotriazole (**154**).<sup>94</sup>



## H. Acylation

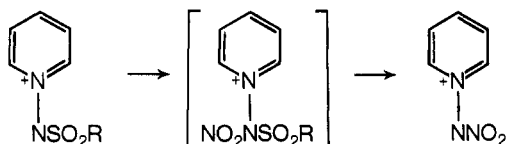
Pyridine-1-benzenesulfonimide, pyridine-1-(2,4,6-trichlorobenzenesulfonimide), and pyridine-1-benzimide

TABLE XXII. Yields of Pyrazolidines (71)

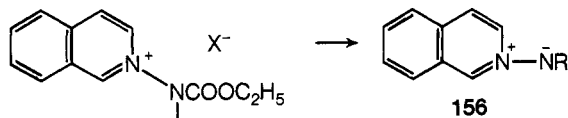
Hydrazide	Aldehyde	Olefin	Yield, %
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	98
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	2-ClC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub>	91
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	4-ClC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub>	75
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	3,4-(CH <sub>3</sub> COO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CH <sub>2</sub>	29
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	CH <sub>2</sub> =CHCH=CH <sub>2</sub>	68
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	CH <sub>2</sub> =CHCOOC <sub>2</sub> H <sub>5</sub>	72.6 <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	CH <sub>2</sub> =CHCN	82 <sup>a</sup>
CH <sub>3</sub> CONHNHCH <sub>3</sub>	CH <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub>	10
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>3</sub>	23
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	Indene	89
RCONHNYCH <sub>3</sub>	CH <sub>2</sub> O	1,2-Dihydronaphthalene	72 <sup>a</sup>
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	Ethyl cinnamate	32 <sup>a</sup>
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	<i>trans</i> -1-Phenyl-1-propene	7
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	Norbornene	50
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	Benzonorbornadiene	91
RCONHNHCH <sub>3</sub>	CH <sub>2</sub> O	1,4-Dihydro-1,4-epoxynaphthalene	87
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	58 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	HCOCOCOC <sub>2</sub> H <sub>5</sub>	Indene	37
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHNHCH <sub>3</sub>	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	43 <sup>b</sup>
CH <sub>3</sub> CONHNHCH(CH <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> CO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	86
CH <sub>3</sub> CONHNHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H <sub>2</sub> CO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	67
CH <sub>3</sub> CONHNHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H <sub>2</sub> CO	Indene	56
CH <sub>3</sub> CONHNH- <i>p</i> -( <i>c</i> -C <sub>6</sub> H <sub>10</sub> )NCH <sub>3</sub>	H <sub>2</sub> CO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	92
CH <sub>3</sub> CONHNH- <i>p</i> -( <i>c</i> -C <sub>6</sub> H <sub>10</sub> )NCH <sub>3</sub>	H <sub>2</sub> CO	Indene	69
CH <sub>3</sub> CONHNHCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> · HCl	H <sub>2</sub> CO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	61
CH <sub>3</sub> CONHNHC <sub>6</sub> H <sub>5</sub>	H <sub>2</sub> CO	Indene	29
C <sub>6</sub> H <sub>5</sub> NHNHCH <sub>3</sub>	H <sub>2</sub> CO	Indene	19

<sup>a</sup> Mixture of isomers. <sup>b</sup> Mixture of *cis*-*trans* isomers.

when treated with nitric acid in a mixture of acetic acid and acetic anhydride gave pyridine-1-nitroimide.<sup>35</sup>

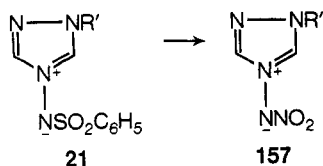


The same type of intermediate (155) is involved in the conversion of isoquinoline-2-carbonylimide by *p*-nitrobenzoyl chloride, *p*-toluenesulfonyl chloride, and cyanogen bromide into the corresponding aminiminides 156<sup>62</sup> and was actually isolated for the first two examples.



- 155**
- a**, R = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO  
**b**, R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>  
**c**, R = CN

1,2,4-Triazole-4-benzenesulfonimides (21) upon treatment with nitric acid in acetic acid-acetic anhydride gave the nitroimide 157<sup>a,b</sup> predominately. The corre-

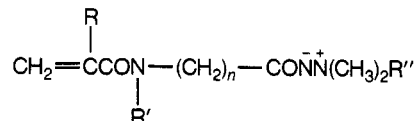


- 21**
- a**, R' = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
**b**, R' = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p*

sponding acetyl derivative **33** (R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>) gave the triazolium nitrate.<sup>133</sup>

## I. Polymerization

Polymers containing the aminimide functional group can be made by polymerizing trimethylamine-methacrylimide,<sup>75</sup> trimethylamine-4-vinylbenzamide,<sup>49</sup> 1,1-dimethyl-1-(2-hydroxypropyl)amine-methacrylimide, 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine-methacrylimide,<sup>81</sup> 1,1-dimethyl-1-(2-hydroxypropyl)amine-*N*-methacryloylglycinimide (**158a**), 1,1-dimethyl-1-(2-hydroxypropyl)amine- $\beta$ -(*N*-cyclohexyl-*N*-acryloyl)aminopropionimide (**158b**), 1,1,1-trimethylamine- $\beta$ -(*N*-phenyl-*N*-acryloyl)aminopropionimide (**158c**), and 1,1-dimethyl-(2-hydroxypropyl)amine-*N*-acryloylglycinimide (**158d**)<sup>77</sup> in aqueous solution using



- 158a**, R = CH<sub>3</sub>; R' = H; R'' = CH<sub>2</sub>CH(OH)CH<sub>3</sub>; n = 1  
**b**, R = H; R' = cyclohexyl;  
R'' = CH<sub>2</sub>CH(OH)CH<sub>3</sub>; n = 2  
**c**, R = H; R' = C<sub>6</sub>H<sub>5</sub>; R'' = CH<sub>3</sub>;  
n = 2  
**d**, R = R' = H; R'' = CH<sub>2</sub>CH(OH)CH<sub>3</sub>;  
n = 1

azobisisobutyronitrile as an initiator. The same reaction with the hydrochlorides of trimethylamine-acrylimide, trimethylamine-methacrylimide,<sup>134</sup> and 1,1-dimethyl-1-(2-hydroxypropyl)amine-methacrylimide<sup>114</sup> gave polymers containing the acyltrialkylhydrazonium chloride group

(133) H. J. Timpe, *Z. Chem.*, **11**, 340 (1971).

(134) B. M. Culbertson and R. C. Fries, *Macromolecules*, **3**, 715 (1970).

TABLE XXIII. Yields of Pyrazolidines (150)

Hydrazide	Benzaldehyde substituent	Yield, %
CH <sub>3</sub> NHNHCOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	92 <sup>a</sup>
CH <sub>3</sub> NHNHCOCH <sub>3</sub>	2-OCH <sub>2</sub> CH=CHCH <sub>2</sub> OH- <i>trans</i>	73 <sup>a</sup>
CH <sub>3</sub> NHNHCOCH <sub>3</sub>	2-OCH <sub>2</sub> CH=CHCH <sub>2</sub> OH- <i>cis</i>	74 <sup>a</sup>
CH <sub>3</sub> NHNHCOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2-N(CHO)CH <sub>2</sub> CH=CH <sub>2</sub>	57
CH <sub>3</sub> NHNHCOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2-O-2-cyclohexene	69 <sup>a</sup>
CH <sub>3</sub> NHNHCOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2-N(CHO)-3-cyclohexene	48
CH <sub>3</sub> NHNHCOCH <sub>3</sub>	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	35
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NHNHCOCH <sub>3</sub>	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	91
N-CH <sub>3</sub> (pip)NHNHCOCH <sub>3</sub> <sup>b</sup>	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	88
CH <sub>3</sub> NHNHC <sub>6</sub> H <sub>5</sub>	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	70
Pyrazolidin-3-one	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	41 <sup>a</sup>

<sup>a</sup> Mixture of stereoisomers. <sup>b</sup> pip = piperidinyI.

TABLE XXIV. Q and e Values of Aminimides and Their Hydrochlorides

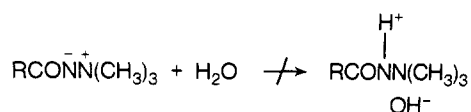
Monomer	Q	e	Ref
CH <sub>2</sub> =CH(CH <sub>3</sub> )CO $\overline{N}$ (CH <sub>3</sub> ) <sub>3</sub>	0.183	-0.60	75
<i>p</i> -H <sub>2</sub> C=CHC <sub>6</sub> H <sub>4</sub> CO $\overline{N}$ (CH <sub>3</sub> ) <sub>3</sub>	0.88	0.31	49
CH <sub>2</sub> =C(CH <sub>3</sub> )CO $\overline{N}$ (CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHCH <sub>3</sub> OH	0.12	-2.45	81
CH <sub>2</sub> =C(CH <sub>3</sub> )CO $\overline{N}$ (CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHOHCH <sub>2</sub> OH	0.24	-1.24	81
CH <sub>2</sub> =CHCONH $\overline{N}$ (CH <sub>3</sub> ) <sub>3</sub> Cl <sup>-</sup>	0.69	0.34	134
CH <sub>2</sub> =C(CH <sub>3</sub> )CONH $\overline{N}$ (CH <sub>3</sub> ) <sub>3</sub> Cl <sup>-</sup>	0.61	0.66	134
CH <sub>2</sub> =C(CH <sub>3</sub> )CONHN(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHOHCH <sub>3</sub> Cl <sup>-</sup>	0.88	0.67	114

which was converted to the aminimide with alkali or a basic ion-exchange resin.

Both types of monomers copolymerized with other common vinyl monomers. The Alfrey-Price Q and e values determined for these possibilities are given in Table XXIV.

#### IV. Physical Properties

The majority of aminimides are crystalline solids which are soluble in water. The resulting solutions are neutral (pH 6.9-7.2) and have a low conductivity.<sup>33,50,64</sup> This property precludes the possibility of the formation of a ionized quaternary ammonium hydroxide.

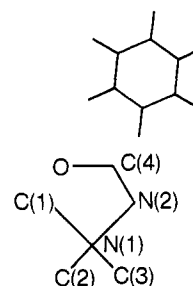


These properties remained essentially unchanged after standing in solution at room temperature or at 50° for 24 hr.<sup>50,64</sup>

#### A. Crystallography

Trimethylamine-benzimide crystals are reported to form in the monoclinic crystal system,  $a = 11.62$ ,  $b = 7.93$ ,  $c = 11.45$  Å,  $\beta = 113.8^\circ$ ,  $Z = 4$ , space group,  $P_1^2/c$ .<sup>135</sup> The solid-state conformation of trimethylamine-benzimide is characterized by the syn-planar relationship within the N(1)-N(2)-C(4)-O system. The comparison of the bond length reveals that the N(1)-N(2) (1.471 (5) Å) distances are similar to single bonds. The N(2)-C(4) (1.313 Å) distances are slightly longer than expected for double bonds, thus indicating significant charge delocalization on the carbonyl atom. The carbonyl bond of (1.243 (5) Å) is slightly longer than expected for bonds where no delocalization occurs.

(135) A. F. Cameron, N. J. Hair, D. G. Morris, and D. M. Hawley, *Chem. Commun.*, 725 (1971).



The crystal data for trimethylamine-*p*-bromobenzimide were reported to be similar. These data are shown in Table XXV.<sup>111</sup>

The geometry about the imide bond is shown for the syn-planar N<sub>11</sub>-N<sub>10</sub>-C<sub>8</sub>-O<sub>9</sub>. The 1.37-Å bond length for the carbonyl carbon imide nitrogen bond shows a significant shortening of the C-N single bond. Along with the planarity of the OCN system, evidence again emphasized favorable geometry for the delocalization of the electron

TABLE XXV. Crystal Data for Trimethylamine-*p*-bromobenzimide

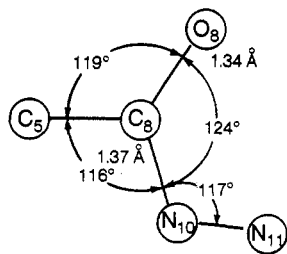
Crystal system	Monoclinic
Lattice parameters	$a = 6.001 \pm 0.012$ Å $b = 13.83 \pm 0.03$ Å $c = 27.63 \pm 0.06$ Å $B = 90.00 \pm 0.33^\circ$
Space group	$P_1^2/c$ ( $C_{2h}^5$ )
Observed systematic absence	$0k0$ $k = 2n + 1$ $h0l$ $l = 2n + 1$ $hkl$ no restrictions
Unit cell volume	229 <sub>3</sub> Å <sup>3</sup>
No. of molecules in unit cell	8
No. of electrons in unit cell	1040
Crystal size	$0.48 \times 0.18 \times 0.21$ mm
Linear absorption coeff	$r = 39.1$ cm <sup>-1</sup>
Density	
Exptl	1.50 g/cm <sup>3</sup>
Calcd	1.46 g/cm <sup>3</sup>

TABLE XXVI. Infrared Frequencies of Acylaminimides

Compound	$\gamma_{\max}$ , $\text{cm}^{-1}$ ( $>\text{C}=\text{O}$ )	Ref
1. $\text{CH}_3\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1590	43
2. $\text{CH}_3\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{C}_{12}\text{H}_{25}$	1575-80	64
3. $\text{CH}_3\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$ -Pyr <sup>a</sup>	1590	22
4. $\text{CH}_3\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2$ - <i>p</i>	1580	39
5. $\text{CH}_3(\text{CH}_2)_{10}\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1575	50
6. 1-Ad- $\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$ <sup>b</sup>	1570	74
7. $\text{CH}_3\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)(\text{C}_6\text{H}_{13})_2$	1580	56
8. $\text{C}_6\text{H}_5\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)(\text{C}_6\text{H}_{13})_2$	1560	56
9. $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1565	45
10. 3-Pyr- $\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$ <sup>a</sup>	1560	74
11. $\text{C}_6\text{H}_5\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1600	112
12. <i>p</i> - $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1575	49
13. $\text{C}_6\text{H}_5\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$ -1-Pyr <sup>a</sup>	1592	21
14. $\text{C}_6\text{H}_5\text{NHCO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1625	59
15. $\text{CH}_3\text{NHCO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1600	59
16. $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1570	60
17. $(\text{C}_6\text{H}_5)_2\text{NCO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1600	60
18. $\text{CH}_3\text{CH}_2\text{OCO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1620	59
19. $\text{C}_6\text{H}_5\text{OCO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1670	59
20. $\text{CF}_3\text{CF}_2\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_3$	1659	74
21. $\text{CH}_3(\text{CH}_2)_{10}\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	1570	80
22. $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	1580	80
23. $\text{C}_6\text{H}_5\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	1580	80
24. 1-Ad- $\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	1570	80
25. 3-Pyr- $\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{CHOHCH}_3$ <sup>a</sup>	1560	80
26. $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{CH}_2\text{CHOHCH}_2\text{OH}$	1550	81
27. $\text{C}_6\text{H}_5\text{C}\equiv\text{CCO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_5$	1600	73
28. $\text{C}_6\text{H}_5\text{CO}\overset{+}{\text{N}}\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_5$	1560	56
29.	1565-1585	58
30.	1550-1600	57
31.	1580	86
32.	1580-1600	85

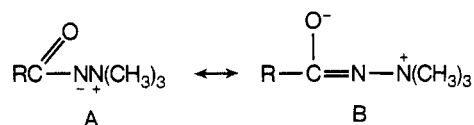
<sup>a</sup> Pyr = pyridyl. <sup>b</sup> Ad = adamantyl.

pair in the p orbital of the imide nitrogen with the  $\pi$  orbital of the carbonyl.



## B. Infrared Spectra

The infrared spectra of acylaminimides show a very strong absorption in the  $1555\text{--}1600\text{-cm}^{-1}$  region which is assigned to the stretching frequency of the  $-\text{OC}=\text{N}$  bond<sup>39,46,73,86</sup> in the resonance form B. This form makes a major contribution to the actual structure since the carbonyl frequency in the protonated form of the aminimide at  $1700\text{ cm}^{-1}$  is completely suppressed.



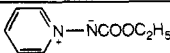
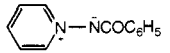
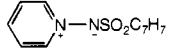
The effect of the group in the acid portion of the aminimide on the absorption is greater than that of the substituents on the cationic nitrogen because of its proximity. In general, derivatives of aliphatic acid (compounds 1-7 in Table XXVI) give absorptions in the range  $1570\text{--}1590\text{ cm}^{-1}$ . Aromatic acid and unsaturated acid derivatives (No. 8-13, Table XXVI) are usually in the range of  $1560\text{ cm}^{-1}$ .

Electron-donating groups in the acid moiety (No. 19), which would favor form A, shift the absorption to higher frequencies. The perfluoroethyl group (No. 20) in agreement with its effect upon the absorption of ketones behaves in a similar fashion.

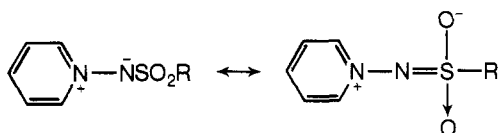
Introduction of groups other than alkyl on the cationic nitrogen (No. 21-30) has a varied effect. Cyclic aminimides (No. 31-32) gave absorptions which were similar to those for the aliphatic derivatives.



TABLE XXVII. Ultraviolet Spectra of Pyridine-1-acylimide<sup>21</sup>

Aminimide	$\lambda_{\max}$ , nm ( $\epsilon$ )	(CH <sub>3</sub> OH)
	228 (6600)	315 (5530)
	233 (13,530)	317 (4850)
	240 (14,000)	317 (2180)

The infrared spectra of pyridine-1-benzenesulfonimides exhibit two strong bands for the SO<sub>2</sub> group in the 1270–1285- and 1130–1140-cm<sup>-1</sup> region. Pyridine-1-methanesulfonimide gave bands at 1270 and 1115 cm<sup>-1</sup>. These frequencies are lower than those for sulfonamides at 1350–1300 and 1180–1140 cm<sup>-1</sup> and suggest a delocalization of the electron pair on the imino nitrogen onto the sulfonyl group.<sup>15</sup>



Trimethylamine-*p*-toluenesulfonimide<sup>31</sup> also gave absorptions at lower frequencies, 1250 and 1126 cm<sup>-1</sup>, for the SO<sub>2</sub> group.

### C. Ultraviolet Spectra

The ultraviolet absorption spectrum of the aminimides, in the commonly accessible region available for spectrometry in the liquid phase, consists of a relatively strong band near 200 nm.<sup>43</sup> The origin of this band is uncertain, but it is probably a  $\pi \rightarrow \pi^*$  transition of the C=O double bond in conjunction with the unbonded electrons on the adjacent nitrogen. This behavior is fairly general for all trialkylamine aminimides. Pyridine-1-acylimides, however, show not only the relatively strong band at >200 nm but have a ultraviolet maximum >304–318 nm.<sup>21,69</sup> Pyridine-1-benzenesulfonimide shows a similar behavior (Table XXVII).

### D. Nuclear Magnetic Resonance

The nmr absorption spectra of trimethylamine-acylimides show a singlet at  $\delta$  3.0–3.4 for the hydrogens of the three methyl groups.<sup>43,49,59,73,74,103</sup> The chemical shift for this group is at a higher field than that ( $-\delta$  3.70) for the corresponding hydrogens in the protonated species.<sup>46,59</sup> Substitution of other alkyl groups for the methyls such as hexyl has little effect on the chemical shift ( $\delta$  3.15–3.18).<sup>56</sup> The introduction of a phenyl group for one of the methyls shifts the singlet to  $\delta$  3.68.<sup>79</sup> 2-Hydroxyalkyl groups behave similarly and give a complex multiplet at 3.80–4.40.<sup>45,75,80,81,91</sup>

The nmr spectra of pyridine-1-carbonylimides, pyridine-1-benzoylimide,<sup>21</sup> pyridine-1-benzenesulfonimides,<sup>15,21</sup> and pyridine-1-methanesulfonimide<sup>15</sup> are complicated and will not be listed.

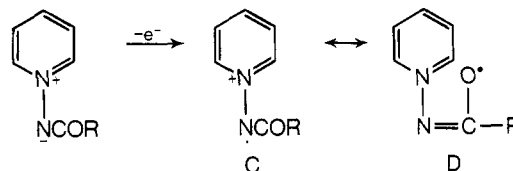
The spectrum of trimethylamine-*p*-toluenesulfonimide<sup>31</sup> is similar to that of the acyl derivatives and exhibited a singlet at  $\delta$  3.18.

### E. Mass Spectra

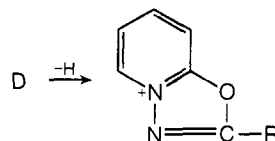
The mass spectra for several acylaminimides have been reported. Trimethylamine-benzimide gave no parent peak, but intense peaks of mass 119 and 59 correspond-

ing to the formation of phenyl isocyanate and trimethylamine were present.<sup>113</sup>

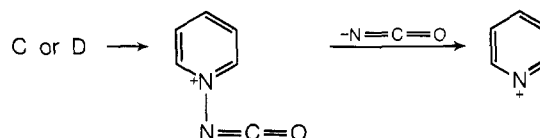
A more intensive study of pyridine-1-acylimides and isoquinoline-2-acylimides<sup>126</sup> found that with three exceptions all compounds gave (M - 1)<sup>+</sup> ions as well as intense molecular ions.



Using deuterated pyridines it was demonstrated that isomer D was the precursor of the (M - 1)<sup>+</sup> ion.

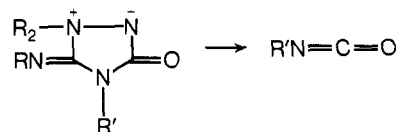


Primary fragmentation was an  $\alpha$  cleavage of the molecular ion C or D as indicated.



Exceptions to this behavior were pyridine-1-carbonylimide and 2,6-dimethylpyridine-1-acylimide (CH<sub>3</sub>CO, C<sub>6</sub>H<sub>5</sub>CO). The first of these lost ethylene and gave pyridine-1-imine; the second fragmented to 2,6-dimethylpyridine 1-oxide.

In the cyclic series the adduct from dialkylaminoisocyanate and dialkylcarbodiimide was found to eliminate isocyanate in the mass spectrometer.<sup>105</sup>



Mass spectral studies<sup>136</sup> of pyridine-1-arenesulfonimides indicate the formation of a molecular ion (M<sup>+</sup>) which with pyridine derivatives form the (M - 1)<sup>+</sup> ions that are the precursors of the (M - HSO<sub>2</sub>) ions (Scheme III). The molecular ion (M<sup>+</sup>) lost SO<sub>2</sub> directly and gave an ion radical (M - SO<sub>2</sub>) which fragmented to smaller species. The molecular ion (M<sup>+</sup>) also fragmented with the formation of a nitrene which eliminated HCN and formed a metastable peak.

The last fragmentation is more important with  $\alpha$ -methylpyridine derivatives and gave nitrenes which lost the CH<sub>3</sub>N radical or HCN (Scheme IV). Loss of sulfur dioxide occurred only from the molecular ion M<sup>+</sup> and gave a species which lost a NH<sub>2</sub> radical and formed a metastable peak. The principal mass spectral peaks for a number of pyridine-1-sulfonimides are shown in Table XXVIII.

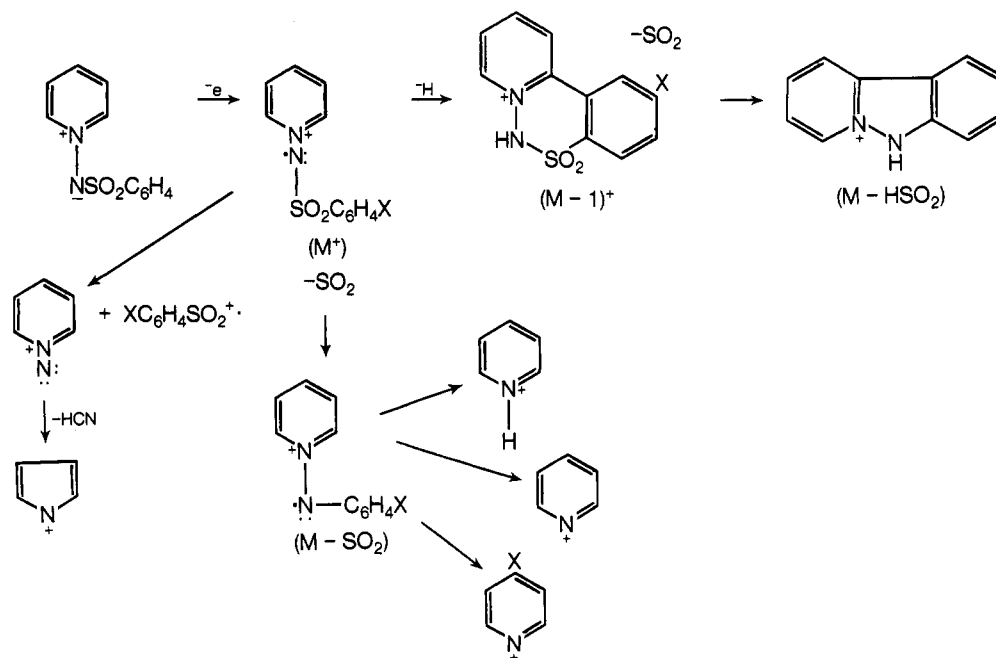
### V. Uses of Aminimides

#### A. Adhesives

Aminimides have been used in a variety of adhesive systems for bonding tire cord, industrial fabrics, wire, and

(136) M. Ikeda, S. Kato, Y. Sumida, and Y. Tamura, *Org. Mass Spectrom.*, **5**, 1383 (1971).

## SCHEME III



## SCHEME IV

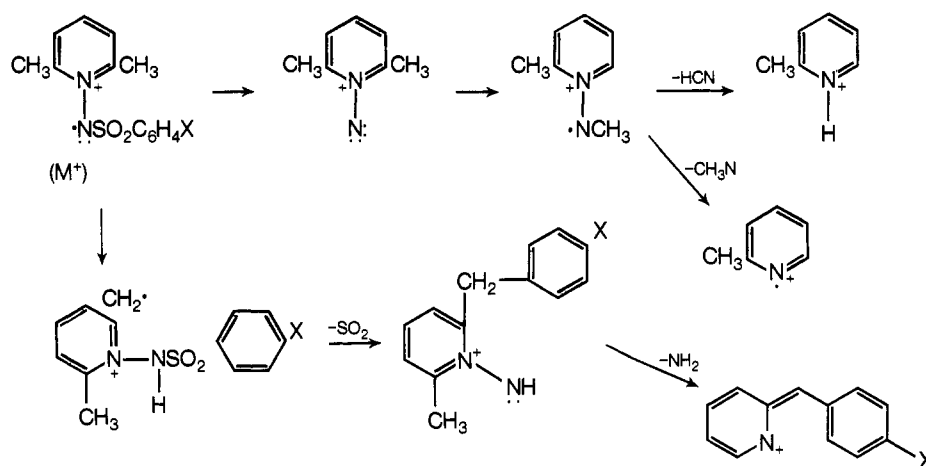
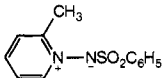
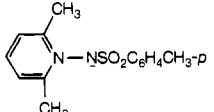
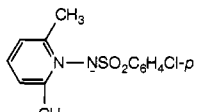


TABLE XXVIII. Principal Mass Spectral Peaks for Pyridine-1-arenesulfonimides (% Relative Intensity)

Aminimide	M <sup>+</sup>	(M - 1) <sup>+</sup>	(M - SO <sub>2</sub> ) <sup>+</sup>	(M - SO <sub>3</sub> H) <sup>+</sup>	Nitrene
C <sub>5</sub> D <sub>5</sub> N <sup>+</sup> -NSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	239 (100)	238, 237 (8) (19)	175 (45)	174, 173 (11) (35)	98 (88)
C <sub>5</sub> H <sub>5</sub> N <sup>+</sup> -NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	248 (56)	247 (13)	184 (50)	183 (21)	93 (61)
C <sub>5</sub> H <sub>4</sub> N <sup>+</sup> -NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	270/268 (22) (59)	269/267 (5) (9)	206/204 (25) (86)	205/203 (4) (14)	93 (100)
	248 (13)		184 (15)	183 (7)	107 (100)
	276 (7)		212 (33)	211 (7)	121 (100)
	298/296 (2) (5)		234/232 (8) (23)	233/231 (1) (4)	121 (100)

glass.<sup>137,138</sup> A typical adhesive for bonding polyester cord to rubber consists of a water solution of a polyfunctional aminimide, an epoxy resin, e.g., Epon 812, and a wetting agent which may be either an anionic or cationic water-soluble surfactant. Polyester cord is dipped into this easily prepared emulsion, and heat treated at 220° for 45–60 sec. The resulting polyester cord is next dipped into an emulsion consisting of resorcinol–formaldehyde resin, a styrenebutadiene–vinylpyridine terpolymer, and formaldehyde at pH 10.5 and heat treated again at 220° for 45–60 sec.

Such an adhesive is safer than that based on phenol-blocked isocyanates since in the thermolysis isocyanates are produced without undesirable by-products such as phenol.

## B. Antistatic Agents

Copolymers from acrylonitrile and acid salts of aminimides derived from acrylic and methacrylic acids show extremely high thermal stability, a high affinity for both acidic and basic dyes, and antistatic properties. The last property facilitates the spinning of these polymers as fibers.<sup>139,140</sup>

## C. Photographic Materials

Acid salts of aminimides when added to light-sensitive silver halide photographic materials behave as antistatic agents with no detrimental effect on the behavior of the film. In addition, it is reported that the salts tend to inhibit fogging and improve the color tone of the developed silver images.<sup>141</sup>

## D. Detergents

Aminimides derived from C<sub>12</sub> through C<sub>18</sub> acids possess interesting surface tension or wetting properties and emulsification characteristics. They behave like nonionic polyoxyethylene surfactants<sup>50,64</sup> with respect to cloud point<sup>142</sup> and exhibit a Krafft point phenomenon similar to that associated with ionic surfactants. Data have also been obtained on the structure and polydispersivity of the micelles formed in aqueous solutions of trimethylamine-tridecanoimide using angular light scattering measurements.<sup>142</sup>

These properties make aminimides of this type useful in standard heavy-duty clothes washing formulations, hard-surface cleaner formulations, and light-duty liquid cleaning formulations.<sup>143,144</sup>

(137) W. J. McKillip, C. N. Impola, and S. F. Chappell, International Rubber Symposium, Paris, France, June 3, 1970.

(138) W. J. McKillip and C. Impola, U. S. Patent 3,628,992; *Chem. Abstr.*, **75**, 77966 (1970).

(139) U. S. Patent 3,414,569; *Chem. Abstr.*, **64**, 9637 (1967).

(140) British Patent 1,166,224; *Chem. Abstr.*, **71**, 113607 (1969).

(141) U. S. Patent 3,549,369; *Chem. Abstr.*, **74**, 125205 (1970).

(142) J. Corkill, K. Gemmill, J. Goodman, and T. Walker, *Trans. Faraday Soc.*, **66**, 1274 (1970).

The excellent detergent properties and low toxicity<sup>145</sup> of aminimides from long-chain acids are the basis for their use in cosmetic products.

## E. Textiles

Polymeric products containing either pendant isocyanate or ethylene-urea groups obtained from pendant aminimides have been shown to be useful in shrink-proofing woolen and worsted fabrics.<sup>146,147</sup>

Application of aminimides of long-chain fatty acids to cellulosic fabrics like rayon or cotton makes these materials water repellent.<sup>50</sup>

Dialkyl- $\beta$ -hydroxyalkylamine-acrylimides are useful as fabric softening agents.<sup>148</sup>

## F. Surface Coatings

Aminimides as precursors of isocyanates have found uses in the field of surface coatings.<sup>149</sup> Polymers prepared from a mixture of vinyl monomers such as styrene, acrylonitrile, or acrylates and aminimides from methacrylic acid have been used in heat-cured thermoset coatings. Formulations of this type cure at 300°F or higher without the addition of melamine, epoxies, or other cross-linked agents. The resulting baked films show a good balance of hardness and flexibility with excellent chemical and solvent resistant qualities.

Such formulations are one-package stable systems which can be used in the conventional solvent paint systems or the emerging acrylic powder coatings.<sup>150</sup>

## G. Elastomers

Mixtures of diaminimides and chain extending polyesters or polyether diols on heating give elastomers.<sup>151</sup>

## H. Pharmaceuticals

Aminimides in the pyrazine series are reported to have antihypertensive, diuretic and saluretic properties.<sup>82</sup> Salts of aminimides have been found to act as antihistamines and anticonvulsants.<sup>152</sup> Aminimides serve as intermediates for the synthesis of imidazolidinones<sup>78</sup> which exhibit potent central nervous system depressant activity in laboratory animals.<sup>153</sup>

(143) U. S. Patent 3,410,880; *Chem. Abstr.*, **70**, 46881 (1969).

(144) German Offen. 2,059,285 (1972).

(145) Independent Laboratory private communication.

(146) W. McKillip, C. Impola, E. Sedor, J. Coyle, W. Fong, and C. Pardo, *Text. Chem. Color.*, **2** (18) (Sept 9, 1970).

(147) U. S. Patent 3,640,676; *Chem. Abstr.*, **75**, 37841 (1971).

(148) German Offen. 2,055,685; *Chem. Abstr.*, **77**, 77095 (1972).

(149) D. D. Taft and A. Mohar, *J. Paint Technol.*, **42**, 550, 615 (1970).

(150) D. D. Taft, R. Hong, and W. J. McKillip, Society of Manufacturing Engineers-Finishing and Coating Technical Paper, C72-942, 1972.

(151) U. S. Patent 3,450,673; *Chem. Abstr.*, **67**, 44289 (1967).

(152) Japanese Patent 40-5631 (1965); *Chem. Abstr.*, **62**, 16206 (1965).

(153) W. Wright, H. Brabander, R. Hardy, Jr., and A. Osterberg, *J. Med. Chem.*, **9**, 852 (1966).