Anal. Calcd for $C_{28}H_{21}NO$: C, 86.8; H, 5.5. Found: C, 86.5; H, 5.5.

Oxidation of the 2*H*-Azepine 17b with *m*-CPBA. A. The azepine **17b**[3,5] (129 mg, 0.335 mmol) was dissolved in chloroform (5 ml) at 25° and *m*-chloroperbenzoic acid (100 mg, 0.66 mmol) was added to the stirred solution. After 1.5 hr the solution was washed with dilute Na_2CO_3 solution and dried over $MgSO_4$. Removal of the solvent gave an oil (135 mg) which rapidly solidified. Recrystallization from chloroform–hexane gave pale yellow-green crystals (79 mg, 59%) of **2-methyl-3,4,7-triphenylbenz[*e*]-2*H*-azepine *N*-oxide (19):** mp 219°; nmr ($CDCl_3$) τ 8.50 (d, J = 7.0 Hz, 3 H), 5.52 (q, J = 7.0 Hz, 1 H), 3.10–2.00 (m, 19 H); ν_{max} (KBr) 1490, 1480, 1445, 1226 (N → O), 780, 757, and 704 cm^{-1}; mass spectrum *m/e* (rel intensity) 401 (100), 385 (32), 384 (79), 369 (10), 359 (14), 357 (19), 356 (20), 343 (11), 324 (25), 285 (37), 284 (41), 283 (13), 280 (19), 278 (12), 270 (11), 269 (17), 268 (59), 267 (13), 265 (15), 252 (17), 290 (12), 165 (14), 117 (10), 115 (18), 105 (40), 91 (19), 83 (11), 77 (34).

Anal. Calcd for $C_{29}H_{23}NO$: C, 86.75; H, 5.8. Found: C, 86.6; H, 5.9.

B. Oxidation of 243 mg (0.635 mmol) of **17b** with 2.62 mmol of the peracid led to quantitative conversion to the *N*-oxide **19** (by tlc). Refluxing of the reaction mixture for 6 hr produced 253 mg of a foam, which on trituration with ether–hexane and recrystallization from chloroform–hexane provided greenish crystals (144 mg, 55%) of **3,4-epoxy-2-methyl-3,4,7-triphenylbenz[*e*]-2*H*-azepine *N*-oxide (21):** mp 231°; nmr ($CDCl_3$) τ 8.62 (d, J = 6.7 Hz, 3 H), 5.45 (q, J = 6.7 Hz, 1 H), 3.05–2.20 (m, 17 H), 2.05–1.80 (m, 2 H); ν_{max} (KBr) 1493, 1446, 1276, 1255, 1236, 770, 760, and 709 cm^{-1}; mass spectrum *m/e* (rel intensity) 417 (11), 359 (11), 270 (13) 268 (15), 165(10), 117 (22), 115 (25), 105 (100), 91 (23) 77 (54).

Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.4; H, 5.55. Found: C, 83.2; H, 5.65.

Oxidation of the Epoxy-2*H*-azepine 20b with *m*-CPBA. Reaction of the epoxide **20b** (300 mg, 0.75 mmol) with the peracid (1.52 mmol) in chloroform (15 ml) for 5 hr afforded a foam (284 mg, 91%) which on trituration with hexane and recrystallization gave the epoxy-2*H*-azepine *N*-oxide **21** (198 mg, 63%), mp 231°, identical in all spectral properties with that obtained in the previous experiment, **17b → 19 → 21.**

Acknowledgment. Support of this research by Grant CA-04474 from the National Cancer Institute is gratefully acknowledged.

Registry No.—1a, 7654-06-0; **1b,** 16205-14-4; **1c,** 18886-64-1; **1d,** 50805-53-3; **2,** 5471-63-6; **3a,** 50805-46-4; **3b,** 34806-16-1; **3c,** 50805-47-5; **3d,** 50805-48-6; **4,** 50805-49-7; **5,** 50805-50-0; **6,** 51018-04-3; **7,** 50805-51-1; **9,** 50883-39-1; **10,** 50805-52-2; **11,** 50805-38-4; **12,** 50805-39-5; **14,** 50805-40-8; **15,** 38274-35-0; **17b,** 39934-15-1; **19,** 50805-41-9; **20a,** 50805-42-0; **20b,** 50805-43-1; **21,** 50805-44-2; **25,** 50805-45-3.

References and Notes

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(21) All melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Nmr spectra were recorded with a Varian A-60A spectrometer using tetramethylsilane as an internal standard. Infrared spectra were taken on a Perkin-Elmer 457 spectrophotometer as KBr pellets. Mass spectra were obtained on a Varian MAT-CH5. The elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga.
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Stevens Rearrangement of Carbamoylaminimides

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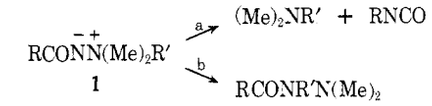
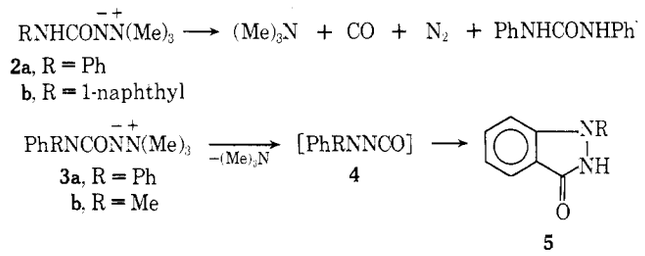
Carbamoylaminimides (**7**) with 1-allyl and 1-benzyl substituents undergo thermal Stevens rearrangements to give semicarbazides (**8**). Thermolysis of 1-(3-methyl-2-butenyl)- and 1-(2-butenyl)aminimides (**9** and **11**) give products resulting from allyl retention, thus ruling out a concerted mechanism for the $N_1 \rightarrow N_2$ allyl rearrangement.

Thermolysis of aminimides derived from carboxylic acids (**1**) has been extensively studied.[1] Isocyanates (or isocyanurates) are obtained from thermolysis of 1,1,1-trimethylamine acylimides[2] and 1-aryl-1,1-dimethylamine acylimides[3] *via* a Curtius-type rearrangement initiated by loss of a tertiary amine (path a). Thermolysis of acylaminimides with 1-allyl[4] and 1-benzyl[5] substituents results in Stevens rearrangement products (path b). Thermolysis of certain 1-benzyl-substituted acylaminimides gives both



Stevens and Curtius products.[6] Products which cannot be rationalized by a Curtius-type mechanism are obtained from thermolysis of 1,1,1-trimethylamine-2-arylcarbamoylimides (**2**). We have found that the major products from the thermolysis of 1,1,1-trimethylamine-2-phenylcar-

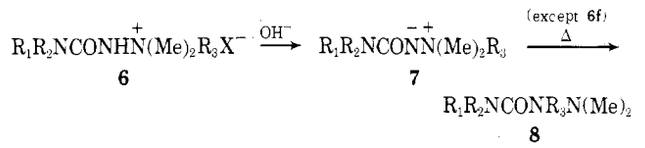
bamoylimide (**2a**) are trimethylamine, nitrogen, carbon monoxide, and 1,3-diphenylurea.[7] A thorough study of the latter has been recently reported by Wawzonek, Plaisance, and Boaz,[8] who identified several minor products from the thermolysis of **2a** and observed analogous results for the 1-naphthyl analog (**2b**). The latter workers also reported that thermolysis of the N,N-disubstituted compounds (**3**) affords indazoles (**5**) which result from cyclization of amino isocyanates (**4**).



This paper reports the results of our study of the thermal Stevens rearrangement of carbamoylaminimides.

The carbamoylaminimides (**7**) were prepared by neutralization of the appropriate 1,1,1-substituted semicarbazonium salts (**6**). The series included carbamoylaminimides with phenylcarbamoyl, *N,N*-dimethylcarbamoyl and *N,N*-diphenylcarbamoyl substituents.

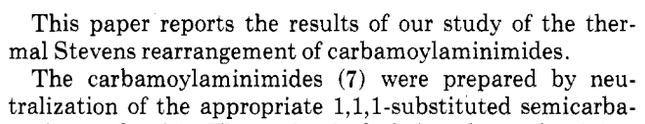
All of the 1-allyl- and 1-benzyl-substituted aminimides underwent thermal Stevens rearrangements to give semicarbazides (**8**). Thermolysis of the propargyl compound (**7f**) gave unidentified tars. No other products could be isolated from these reactions, thus indicating that the thermolysis pathway for these compounds is apparently not dependent on the carbamoyl substituents as was observed for **2** and **3**. The properties of the semicarbazides (**8**) obtained from the thermal rearrangements are given in Table III. In most instances these compounds were also prepared by carbamoylation of the appropriate trisubstituted hydrazine.

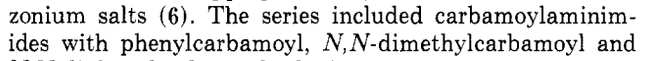


a. $R_1 = R_2 = Me$; $R_3 = CH_2CH{=}CH_2$
b. $R_1 = R_2 = Me$; $R_3 = CH_2Ph$
c. $R_1 = R_2 = Ph$; $R_3 = CH_2CH{=}CH_2$
d. $R_1 = Ph$; $R = H$; $R_3 = CH_2CH{=}CH_2$
e. $R_1 = Ph$; $R = H$; $R_3 = CH_2Ph$
f. $R_1 = Ph$; $R = H$; $R_3 = CH_2C{\equiv}CH$

The Stevens rearrangement of allyl-substituted aminimides may proceed by either an allowed concerted [2,3] suprafacial rearrangement or by a nonconcerted radical dissociation–recombination pathway. Baldwin, Brown, and Cordell[9] have reported convincing evidence for a radical mechanism in the Stevens rearrangement of 1-allylic-substituted acylaminimides. Radical trapping[10] and CIDNP[11] have also been employed to support a radical process in the rearrangement of 1-benzyl-substituted acylaminimides.

We have conducted experiments that rule out a simple concerted process for the Stevens rearrangement of 1-allyl-substituted carbamoylaminimides. The 1-(3-methyl-2-butenyl) compound (**9**) was found to thermally rearrange with complete allyl retention to give **10**. Thermolysis of the 1-(2-butenyl) compound (**11**) afforded a mixture that contained 1,1-dimethyl-2-(2-butenyl)-4-phenylsemicarbazide (**12**) and 1,1-dimethyl-2-(1-methyl-2-propenyl)-4-phenylsemicarbazide (**13**) in a ratio of 1:3. Both **12** and **13** were synthesized by the reaction of phenyl isocyanate with the appropriate trisubstituted hydrazine and were found to be stable at 145° (thermolysis temperature) and 185°. Although our results do not lend themselves to detailed mechanistic interpretation (except to exclude a concerted process) the radical dissociation–recombination pathway proposed by Baldwin, Brown, and Cordell[9] could satisfactorily account for the results. The formation of both **12** and **13** in the thermolysis of **11** could be accounted for by assuming competitive concerted and radical processes[12] or by recombination of the radical pair **14** at both





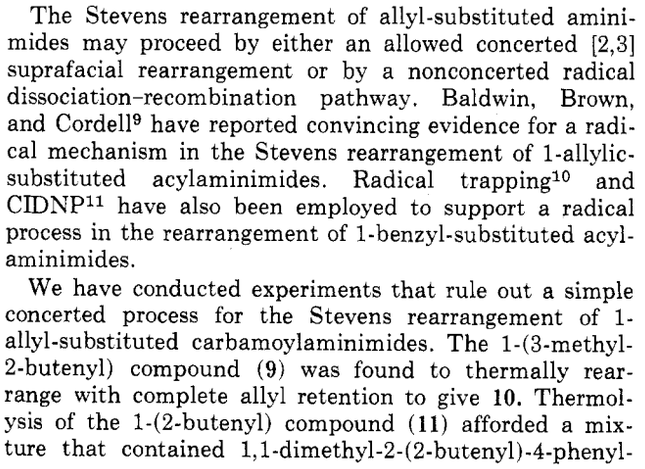
the 1 and 3 positions of the crotyl radical. The exclusive formation of **10** from the thermolysis of **9** could be accounted for by selective recombination of the radical pair to give the more stable allylic isomer.[13]

The formation of products resulting from both allylic inversion and retention has also been reported for 1-(2-butenyl)-1,1-dimethylamine-2-acetimide[14] and 1-(3-phenyl-2-propenyl)-1,1-dimethylamine-2-acetimide.[15]

Further evidence to support a radical process for these allylic rearrangements was not obtained from CIDNP experiments on **7a**. Compound **7a** failed to give evidence of CIDNP at 104° ($t_{1/2}$ *ca.* 9 min) or 127° ($t_{1/2}$ 1–2 min). Failure to observe CIDNP with this compound does not preclude a radical process for its rearrangement to **8a**.[16]

Compound **7a** was recovered unchanged after irradiation[17] in benzene.

Reaction of crotyl bromide with 1,1-dimethyl-4-phenylsemicarbazide repeatedly gave low yields of an insoluble salt whose analytical and spectral[18] properties seem to be best accommodated by either a symmetrically substituted dimer[19] (**16**) or trimer (**17**) of the quaternary isocyanate (**18**). Compound **18** could form by elimination of aniline from **15**. Infrared evidence (carbonyl bands at 1690 and 1740 cm^{-1}) excludes **18** from consideration. Analogous behavior in the reaction of other semicarbazides with allylic halides was sought but not found.



R = $CH_2CH{=}CHMe$

Table I
Semicarbazonium Salts (6)[a]

$R_1R_2NCONHN^+(Me)_2R_3X^-$

Structure	Mp, °C	Recrystn solvent	Yield, %	Formula	Nmr, δ
6a Br^-	105-106	Acetone	94	$C_8H_{18}BrN_3O$	2.94 (s, 6), 3.79 (s, 6), 4.86 (d, 2), 5.5–5.9 (m, 3), 9.6 (s, 1) ($CDCl_3$)
6b Br^-	155–156	Acetone	82	$C_{12}H_{20}BrN_3O$	3.71 (s, 6), 2.98 (s, 6), 5.40 (s, 2), 9.9 (broad, 1), 7.20–7.60 (m, 5) ($CDCl_3$)
6d Br^-	76–78	EtOH–ether	94	$C_{12}H_{18}BrN_3O$	3.56 (s, 6), 4.60 (d, 2), 5.69 (m, 3), 7.33 (m, 5), 9.47 (s, 1), 10.0 (broad, 1) (DMSO-d_6)
6e Cl^-	133–135	Acetone	51	$C_{16}H_{20}ClN_3O$	3.58 (s, 6), 5.18 (s, 2), 6.7–7.5 (m, 10), 9.8 (s, 1), 10.74 (broad, 1) (DMSO-d_6)
6f Br^-	151-153	EtOH	68	$C_{12}H_{16}BrN_3O$	3.68 (s, 6), 4.08 (t, 1), 5.08 (d, 2), 6.9–7.4 (m, 5), 9.53 (s, 1), 10.2 (s, 1) (DMSO-d_6)
9 HCl[b]	50–58 (hygroscopic)		70	$C_{14}H_{22}ClN_3O$	1.68 (s, 3), 1.73 (s, 3), 3.51 (s, 6), 4.5 (d, 2), 5.35 (m, 1), 6.8–7.4 (m, 5), 9.84 (s, 1), 10.66 (s, 1) (DMSO-d_6)
15	Hygroscopic oil		90	$C_{13}H_{20}BrN_3O$	1.7 (d, 3) 3.5 (s, 6), 5.3–6.3 (m, 2), 4.45 (d, 2), 7.1-7.4 (m, 5), 9.33 (s, 1, NH), 9.7 (s, 1 NH) (DMSO-d_6)

[a] Compounds **15** and **9** HCl did not give satisfactory analyses. Other compounds analyzed satisfactorily (±0.3%) for C, H, and N. [b] Tabulated as aminimide salt.

Table II
Aminimides (7)[a]

$R_1R_2NCON\bar{N}(Me)_2R_3$

Structure	Yield, %	Mp, °C	Formula	Nmr, δ
7a	100	Hygroscopic solid	$C_8H_{17}N_3O$	2.62 (s, 6), 3.19 (s, 6), 4.2 (d, 2), 5.10–5.95 (m, 3) ($CDCl_3$)
7b	52	128–129	$C_{12}H_{15}N_3O$	2.72 (s, 6), 3.11 (s, 6), 4.69 (s, 2), 7.26 (s, 5) ($CDCl_3$)
7c	91	93–94	$C_{18}H_{21}N_3O$	3.05 (s, 6), 3.95 (d, 2), 5.0–5.8 (m, 3), 6.7-7.4 (m, 10) ($CDCl_3$)
7d	100	128–130	$C_{12}H_{17}N_3O$	3.15 (s, 6), 4.15 (d, 2), 5.1–6.3 (m, 3), 6.5–7.4 (m, 6) ($CDCl_3$)
7e	83	145–148	$C_{16}H_{19}N_3O$	3.45 (s, 6), 5.03 (s, 2), 6.8–7.4 (m, 10), 9.64 (broad, 1) (DMSO-d_6)
7f	95	117–118	$C_{12}H_{15}N_3O$	3.21 (s, 6), 3.58 (t, 1), 4.60 (d, 2), 6.3-7.5 (m, 6) ($CDCl_3$)
9	72	155–156	$C_{14}H_{21}N_3O$	1.68 (s, 3), 1.72 (s, 3), 3.11 (s, 6), 4.20 (d, 2), 5.3 (m, 1), 6.18 (s, 1), 6.8–7.4 (m, 5) ($CDCl_3$)
11	40	128–130	$C_{13}H_{19}N_3O$	1.65 (d, 3), 3.11 (s, 6), 4.05 (d, 2), 5.6 (m, 2), 6.20 (s, 1), 6.6–7.3 (m, 5) ($CDCl_3$)

[a] With the exception of **7a**, all compounds gave satisfactory (±0.3%) analyses for C and H.

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. Nmr spectra were determined with a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as the internal standard.

1,1,4,4-Tetramethylsemicarbazide. *N,N*-Dimethylcarbamoyl chloride (107.5 g) was slowly added to a stirred, ice-cooled solution containing 60.1 g of 1,1-dimethylhydrazine and 101.2 g of triethylamine in 400 ml of dry benzene. After the addition was complete, stirring was continued for 1 hr at room temperature. The triethylamine hydrochloride was filtered off and washed with dry benzene. Evaporation of the filtrate and combined washings gave 139.5 g of product that crystallized on standing: bp 131–133° (26 mm); mp 68–70°; nmr ($CDCl_3$) δ 2.51 (s, 6), 2.81 (s, 6), 6.4 (broad, 1).

Anal. Calcd. for $C_5H_{13}N_3O$: C, 45.8; H, 10.0; N, 32.0. Found: C, 45.5; H, 9.6; N, 32.0.

Synthesis of Semicarbazonium Salts (6). Equimolar mixtures of either 1,1,4,4-tetramethylsemicarbazide, 1,1-dimethyl-4,4-diphenylsemicarbazide,[8] or 1,1-dimethyl-4-phenylsemicarbazide[8] and the appropriate halide were heated on the steam bath under reflux for 1–2 hr. The cooled reaction mixtures were treated with dry ether and scratched to induce crystallization. The properties of the salts are given in Table I. The reaction of 1,1-dimethyl-4,4-diphenylsemicarbazide with allyl bromide gave a gum that was not characterized but converted directly to **7c**. Treatment of 1-(2-butenyl)-1,1-dimethyl-4-phenylsemicarbazonium bromide

Table III
Semicarbazides (8)[a]

$R_1R_2NCONR_3N(Me)_2$

Structure	Thermolysis conditions	Mp (recrystn solvent) or bp, °C (mm)	Yield,[b] %	Formula	Nmr, δ
8a	130° (2.5 hr)	110–120 (20)	41 (T)[c] 22 (S)	$C_8H_{17}N_3O$	2.36 (s, 6), 2.78 (s, 6), 3.67 (d, 2), 4.7–6.1 (m, 3) (neat)
8b	165° (3.5 hr)	98–99 (ligroin)	63 (T) 39 (S)	$C_{12}H_{19}N_3O$	2.41 (s, 6), 2.79 (s, 6), 4.13 (s, 2), 7.17 (s, 5) ($CDCl_3$)
8c	135° (1 hr)	133–134[d] (EtOH)	69 (T) 47 (S)	$C_{24}H_{24}N_6O_8$[d]	2.28 (s, 6), 3.80 (d, 2) 4.8–5.3 (m, 3), 6.5–7.4 (m, 10), 7.70 (s, 1, NH), 8.5 (s, 2) (DMSO-d_6)
8d	150° (3 hr)	190–194 (22)	40 (T) 100 (S)[e]	$C_{12}H_{17}N_3O$	2.42 (s, 6), 3.86 (d, 2), 4.8–6.4 (m, 3), 6.7–7.7 (m, 5), 8.90 (s, 1) (DMSO-d_6)
8e	175° (1 hr)	76–77 (EtOH)	62 (T) 73 (S)	$C_{16}H_{19}N_3O$	3.6 (s, 6), 5.38 (s, 2), 6.9–7.7 (m, 10), 9.18 (s, 1) ($CDCl_3$)
10	160° (1.5 hr)	45–47 (ligroin)	50 (T)	$C_{14}H_{21}N_3O$	1.58 (s, 6), 2.41 (s, 6), 2.87 (d, 2), 5.20 (m, 1), 6.6–7.5 (m, 5), 8.48 (s, 1) ($CDCl_3$)
12		83–84 (ligroin)	53 (S)	$C_{13}H_{19}N_3O$	2.60 (m, 3), 2.40 (s, 6), 3.85 (m, 2), 5.5 (m, 2), 6.7–7.5 (m, 5), 8.48 (s, broad, 1) ($CDCl_3$)
13		142–145 (0.05)	53 (S)	$C_{13}H_{19}N_3O$	1.36 (d, 3), 2.37 (s, 6), 3.9 (m, 1), 5.0 (m, 2), 6.20 (m, 1), 6.8–7.6 (m, 5), 8.71 (s, 1) (DMSO-d_6)

[a] All compounds gave satisfactory (±0.4%) analyses for C and H. [b] Yields of recrystallized or distilled products. [c] T = thermolysis product; S = synthetic product. [d] Picrate. [e] Undistilled product (identical with thermolysis product).

and 1-(3-methyl-2-butenyl)-1,1-dimethyl-4-phenylsemicarbazonium bromide (both hygroscopic) with ethanolic picric acid resulted in precipitation of **1,1-dimethyl-4-phenylsemicarbazide picrate.** Recrystallization from *N,N*-dimethylformamide–water gave yellow crystals, mp 197–198°.

Anal. Calcd for $C_{15}H_{16}N_6O_8$: C, 44.2; H, 4.0. Found: C, 44.2; H, 4.3.

Reaction of 1,1-Dimethyl-4-phenylsemicarbazide with Crotyl Bromide. The reaction was conducted as described in the previous section. Treatment of the crude dark reaction mixture with dry acetone (10 ml/g of semicarbazide) gave white crystals (1.6 g from 10 g of semicarbazide), mp 231–234°. The oily, hygroscopic semicarbazonium salt was obtained by evaporation of the acetone and could not be induced to crystallize. The acetone-insoluble material (**16** or **17**) was recrystallized from acetone–pentane: mp 235–236°; nmr (DMSO-d_6) δ 1.75 (m, 3), 3.45 (s, 6), 4.90 (m, 2), 6.50 (m, 2); ir (KBr) 1690 and 1740 cm^{-1} (s, C=O); *m/e* (20 eV, 200°) highest mass 140 ($C_7H_{13}N_2O^+ - 1$).

Anal. Calcd for $(C_7H_{13}BrN_2O)_n$: C, 38.0; H, 5.9; Br, 36.1; N, 12.7. Found: C, 37.8; H, 5.8; Br 35.9; N, 12.7.

Preparation of Aminimides. The semicarbazonium salts were treated with excess 6 *N* NaOH (2 ml/g of salt) and the aminimides were extracted with chloroform. The combined extracts were dried ($MgSO_4$). Evaporation of the solutions at reduced pressure gave the aminimides (Table II). Compound **7a** was obtained as an extremely hygroscopic solid that did not give satisfactory analytical data.

Thermolysis of the Aminimides. Thermolyses of neat samples of the aminimides were conducted under the conditions given in Table III. The composition of the mixture obtained from the thermolysis of the 1-(2-butenyl) compound (**11**) was determined by comparison of the integrated intensity ratios of the –CH=CH– and $=CH_2$ signals of the nmr spectra of **12** and **13**, respectively. The nmr spectrum of the mixture was found to be identical with the additive spectrum of authentic samples of **12** and **13**.

1,1-Dimethyl-2-(2-butenyl)hydrazine. A solution containing 15.0 g of crotonaldehyde *N,N*-dimethylhydrazone[20] in 100 ml of dry ether was added over 1.5 hr to a stirred suspension of 13 g of lithium aluminum hydride in 150 ml of dry ether. The reaction mixture was heated under reflux for 5 hr and then stirred at room temperature for 12 hr. Shorter reaction times and lower concentrations of hydride gave a product that was contaminated (by glc) with starting material. The reaction mixture was cooled in ice, stirred vigorously, and cautiously treated successively with 6 ml of water, 6 ml of 6 *N* NaOH, and 18 ml of water. The inorganic material was filtered off and washed with ether. The filtrate and combined washings were dried ($MgSO_4$) and the ether was removed by distillation at atmospheric pressure. The product was distilled through a 24-in. Vigreux column, giving 10.0 g of product as a colorless liquid: bp 131–133°; nmr ($CDCl_3$) δ 3.05 (m, 3), 2.10 (broad, exchangeable, 1), 3.31 (s, 6), 3.22 (m, 2), 5.45 (m, 2), minor impurities at 2.7 (m), 2.60 (s), and 2.78 (s). The compound rapidly darkened and did not give a satisfactory analysis.

The hydrazine was converted to **1,1,1-trimethyl-2-(2-butenyl)hydrazinium iodide** by reaction with methyl iodide. The salt was obtained as air-sensitive white crystals which were recrystallized from ethanol: mp 188–189°; nmr ($CDCl_3$) δ 1.63 (broad d, 3), 3.58 [s $(Me)_3N^+$ superimposed on the $-CH_2N<$ multiplet, 11], 5.5 (m, 2), 6.41 (m, 1, NH).

Anal. Calcd for $C_7H_{17}N_2I$: C, 32.8; H, 6.7; N, 10.9. Found: C, 33.0; H, 6.5; N, 11.0.

1,1-Dimethyl-2-(1-methyl-2-propenyl)hydrazine. We were unable to prepare the hydrazine by rearrangement of 1,1-dimethyl-1-(2-butenyl)hydrazinium bromide in aqueous sodium hydroxide.[21] Cordell[22] has reported the preparation of an impure product by rearrangement of the hydrazinium salt in ethanolic potassium *tert*-butoxide. The following procedure also afforded a crude product that when treated with phenyl isocyanate gave **13** in 53% yield.

A suspension of 11.4 g of crude 1,1-dimethyl-1-(2-butenyl)hydrazinium bromide[23] in 140 ml of dry ether was vigorously stirred under nitrogen and treated with 47 ml of a 1.7 *M* *n*-butyllithium–hexane solution by dropwise addition conducted over 2 hr. Stirring was continued overnight and the reaction mixture was cautiously treated with 20 ml of water. The layers were separated, the aqueous layer was extracted with ether, and the combined ether solution was dried ($MgSO_4$). The solvents were removed by distillation through a Vigreux column. Distillation of the residue gave a wide-boiling, colorless fraction, bp 80–110°. A sample with bp 109° gave the following nmr data (neat): δ 0.98 (d, *J* = 7 Hz, 3), 2.28 [s (superimposed on a broad NH), 7], 3.30 (m, 1), 4.9 (m, 2), 5.6 (m, 1); impurities in low concentration; 1.82 (s), 2.70 (s), and 0.5–1.8 (m).

Synthesis of Semicarbazides (Table III). 1,1,-Dimethyl-2-

benzylhydrazine and 1,1-dimethyl-2-(2-propenyl)hydrazine were prepared by the published procedure.[24]

The preparation of compounds **8d, 8e, 12,** and **13** was accomplished by treating phenyl isocyanate with an equimolar quantity of the appropriate hydrazine.

Compounds **8a, 8b,** and **8c** were prepared by heating a mixture of either dimethylcarbamoyl chloride or diphenylcarbamoyl chloride with 2 equiv of the appropriate hydrazine at 100° for 1–2 hr. The products were isolated by extracting the crude reaction mixture with boiling petroleum ether.

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Registry No.—6a, 51433-78-4; **6b,** 51433-77-3; **6c,** 51433-50-2; **6d,** 51433-51-3; **6e,** 51433-52-4; **6f,** 51433-53-5; **7a,** 51433-54-6; **7b,** 51433-55-7; **7c,** 51433-56-8; **7d,** 51433-57-9; **7e,** 51433-58-0; **7f,** 51433-59-1; **8a,** 51433-60-4; **8b,** 51433-61-5; **8c,** 51433-63-7; **8d,** 51433-64-8; **8e,** 51433-65-9; **9,** 51433-66-0; **9** hydrochloride, 51472-52-7; **10,** 51433-67-1; **11,** 51433-68-2; **12,** 51433-69-3; **13,** 51433-70-6; **15,** 51433-71-7; **18,** 51433-76-2; allyl bromide, 106-95-6; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; 3-propynyl bromide, 106-96-7; 1,1,4,4-tetramethylsemicarbazide, 27827-93-6; *N,N*-dimethylcarbamoyl chloride, 79-44-7; 1,1-dimethylhydrazine, 57-14-7; 1,1-dimethyl-4,4-diphenylsemicarbazide, 37934-75-1; 1,1-dimethyl-4-phenylsemicarbazide, 6297-20-7; 1-(2-butenyl)-1,1-dimethyl-4-phenylsemicarbazonium bromide, 51433-71-7; 1-(3-methyl-2-butenyl)-1,1-dimethyl-4-phenylsemicarbazonium bromide, 51472-53-8; 1,1dimethyl-4-phenylsemicarbazide picrate, 51433-72-8; crotyl bromide, 4787-77-4; 1,1-dimethyl-2-(2-butenyl)hydrazine, 51433-73-9; crotonaldehyde *N,N*-dimethylhydrazone, 74422-95-9; 1,1,1-trimethyl-2-(2-butenyl)hydrazinium iodide, 51433-74-0; 1,1-dimethyl-2-(1-methyl-2-propenyl)hydrazine, 15848-66-5; phenyl isocyanate, 103-71-9; 1,1-dimethyl-1-(2-butenyl)hydrazinium bromide, 27828-89-3; *N,N*-diphenylcarbamoyl chloride, 83-01-2; 1,1-dimethyl-2-(2-propenyl)hydrazine, 2736-72-3; 1,1-dimethyl-2-benzylhydrazine, 28082-45-3.

References and Notes

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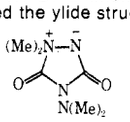
(15) J. E. Brown, Ph.D. Thesis, The Pennsylvania State University, 1971, p 86.
(16) For a recent review of CIDNP and its interpretation when applied to rearrangements of aminimides, see A. R. Lepley in "Chemically Induced Dynamic Nuclear Polarization," A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N. Y., 1973, p 356.
(17) A 450-W Hanovia medium-pressure mercury arc lamp (Pyrex filter) was employed.
(18) The mass spectrum of the salt did not display high mass ion radicals corresponding to cations **16** or **17.** The highest mass peak observed was *m/e* 140, which corresponds to the monomeric cation (**18**) − 1. Depolymerization of **16** or **17** on electron impact apparently occurs. We have found that the mass spectrum of triphenyl isocyanaurate displays $C_6H_5NCO{\cdot}^+$ as the parent peak together with a $(C_6H_5NCO)_3{\cdot}^+$ peak which is 50% less intense.
(19) Dimethylamino isocyanate does not form a diazetidinedione dimer. W. S. Wadsworth and W. D. Emmons [*J. Org. Chem.*, **32,** 1279 (1967)] have established the ylide structure (i) shown below for the



i

dimethylamino isocyanate dimer. The nmr spectrum of the salt obtained by us displays equivalent methyl and crotyl groups; hence a dialkylated derivative of i can be excluded.
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1-Oxadecalins and 1-Oxa-4-decalones. Syntheses and Conformational Analyses

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A general synthetic route to 6- and 7-carbomethoxy-*trans*-1-oxadecalins (**9** and **12**) is presented. Base-catalyzed equilibrations and pmr data are used to evaluate conformational equilibria and relative configurations in several *cis*- and *trans*-1-oxadecalins and 1-oxa-4-decalones. The trans-fused ring system is thermodynamically favored in all instances.

The *trans*-decalin ring system has often been used as a conformationally fixed system for the study of the relative reactivities of equatorial and axial substituents[1] and the relative energies of substituents in a pair of equatorial and axial orientations at a given carbon atom.[2] Similarly, analogs of *trans*-decalin containing an atom other than carbon at a known position in the ring not containing the attached substituents provide the opportunity to evaluate the influences of the heteroatoms on the relative reactivities and relative energies of the substituents. These effects