to afford a small yield of green oil **11h** which darkened on standing: mass spectrum (70 eV) *m/e* 119, 79, 57, 49, 47, 44, 26; ir ($CHCl_3$) 2285 (CN), 2205 (CN), 1685 cm^{-1} (1,4-dihydropyridines); uv max ($CHCl_3$) 243, 290 nm (sh).

1-Carboethoxymethyl-4-cyano-1,4-dihydropyridine (11i). Ethyl chloroacetate and pyridine were combined in THF to yield **10i**. Sodium cyanide (0.7 g, 14 mmol) and 2.8 g (14 mmol) of **10i** were allowed to react as above to furnish a small amount of green oil **11i** which darkened on standing: mass spectrum (70 eV) *m/e* 192 (M^+), 191, 166, 163, 138, 119, 105, 93, 29, 26; ir ($CHCl_3$) 2270 (CN), 1740 (C=O), 1685 cm^{-1} (1,4-dihydropyridine); uv max ($CHCl_3$) 243, 290 nm (sh).

1-Carboethoxy-2-cyano-1,2-dihydropyridine (12a). A solution of 6.3 g (80 mmol) of pyridine and 12.0 g (245 mmol) of sodium cyanide in 40 ml of water was layered with 60 ml of methylene chloride. After the mixture was purged with nitrogen for 5 min, 17.5 g (163 mmol) of ethyl chloroformate was added dropwise (*ca.* 20 min) under nitrogen with stirring. The resulting mixture was stirred for an additional 1 hr, poured into 200 ml of water, and extracted with 200 ml of ether. The extract was concentrated under vacuum, poured into dilute hydrochloric acid (*ca.* 10^{-3} *M*), and extracted with ether. The ether solution was washed with saturated sodium bicarbonate and water, dried, and concentrated under vacuum to afford 3.5 g (25%) of **12a** as a red liquid: ir ($CHCl_3$) 1720 (C=O), 1650 cm^{-1} (1,2-dihydropyridine); uv max ($CHCl_3$) 304 nm; nmr ($CDCl_3$) τ 8.70 (t, 3, J = 7.0 Hz), 5.65 (q, 2, J = 7.0 Hz), 4.35 (m, 3), 3.75 (m, 1) 3.00 (d, 1, J = 7.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 178 (M^+, 6), 105 (32), 79 (100), 78 (61).

Anal. Calcd for $C_9H_{10}N_2O_2$: C, 60.67; H, 5.62. Found: C, 60.17; H, 5.74.

Registry No.—**10a**, 22752-98-3; **10b**, 4185-69-7; **10c**, 26154-94-9; **10d**, 51364-78-4; **10e**, 51364-79-5; **10f**, 13958-90-2; **10g**, 51364-80-8; **10h**, 17281-59-3; **10i**, 27032-03-7; **11a**, 51364-81-9; **11b**, 51364-82-0; **11c**, 51364-83-1; **11d**, 51381-70-5; **11e**, 51364-84-2; **11f**, 51364-85-3; **11g**, 51364-86-4; **11h**, 51364-87-5; **11i**, 51364-88-6; **12a**, 51364-89-7.

References and Notes

(1) (a) Taken in part from the Ph.D. Thesis of R. H. R., Drexel University, 1972. (b) NSF Predoctoral Fellow, 1968–1971. (c) Address all correspondence to this author at Department of Chemistry, Virginia Commonwealth University, Academic Center, Richmond, Va. 23220.
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(29) Solutions of **10a** hydrochloride and sodium bicarbonate precipitated an amorphous brown sludge.
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Cycloaddition of 1-Azirines to 1,3-Diphenylisobenzofuran and Rearrangement of the Adducts[1]

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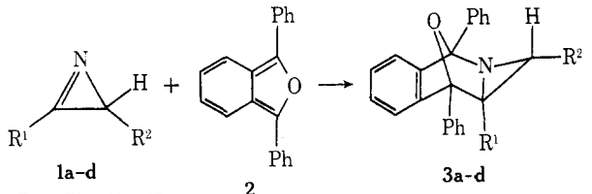
1-Azirines **1** and 1,3-diphenylisobenzofuran (**2**) react smoothly and efficiently in refluxing toluene to afford the simple 1:1 adducts **3**, possessing the exo configuration. Two of the adducts, **3a** and **3b**, were found to rearrange in the presence of neutral alumina, to give the epoxybenzo-2*H*-azepines **20a** and **20b**. Chemical reactions (water, alcohol, $LiAlH_4$) of the adducts **3** generally involved initial opening of the oxido bridge in a regiospecific manner. When more vigorous conditions were used, rupture of the aziridine ring usually followed.

The role of 1-azirines **1** as dienophilic components in Diels–Alder reactions with cyclopentadienones has recently been demonstrated and developed by us[2-5] and others.[6] The products were 3*H*- or 2*H*-azepines but only indirect evidence for the intermediacy of Diels–Alder adducts (7-norbornanones) was obtained. In an effort to isolate related Diels–Alder adducts, we examined, concurrently with our investigations of the cyclopentadienone system, 1,3-diphenylisobenzofuran (**2**) as the diene component. In the meantime a note has appeared[7] on this very same reac-

tion. We describe here our detailed results on the reaction of **1a–d** with **2**, and a novel rearrangement of some of the initial adducts **3**, catalyzed by neutral alumina.

Results and Discussion

A. Structures. When azirines **1a–d** and isobenzofuran **2** were allowed to react in refluxing toluene for 2–24 hr, the 1:1 adducts **3a–d** were obtained in 80–90% yield. The



1a–d **2** **3a–d**

a, $R^1 = Ph$; $R^2 = H$
b, $R^1 = Ph$; $R^2 = Me$
c, $R^1 = H$; $R^2 = Ph$
d, $R^1 = H$; $R^2 = t\text{-Bu}$

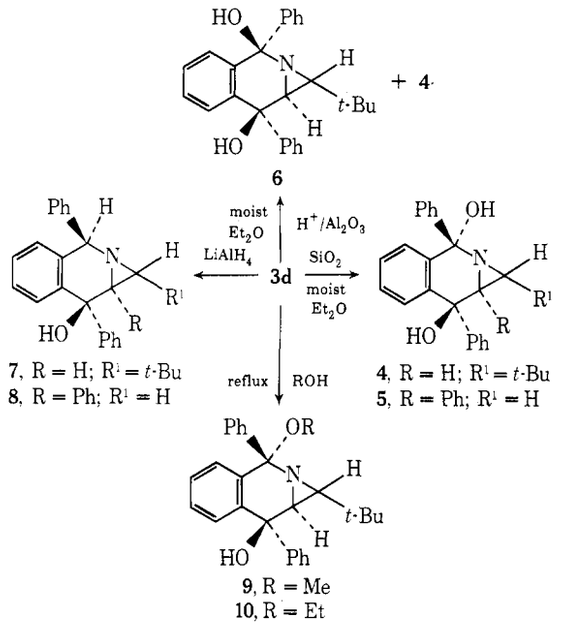
products were thermally stable in refluxing toluene (for 15 days) and though unstable to neutral alumina (see below), they could be purified by passage through a column of Merck acid-washed alumina. The structures of **3** were assigned in analogy with **3b**[7] and on the basis of spectra and chemical reactions.[8] For instance, the low-field position (τ 6.48) of the quartet in **3b** indicated considerable deshielding of this portion by the oxido bridge,[9] demonstrating the exo relationship. Similar deshielding effects have been observed[10-14] in cyclopropene adducts of **2**. The nmr analyses of the other adducts, **3a**, **3c**, and **3d**, contributed additional structure proof for the exo configuration. For example, the singlets at τ 7.70 and 6.66 in **3a**, although unresolved even at 100 MHz, were coupled ($J_{gem} < 0.2$ Hz) as indicated by the fact that irradiation of either peak did cause an increase in the amplitude of the other. It is well known[15,16] that geminal coupling in aziridines is low (0–2 Hz). The adducts **3c** and **3d** (formed by the *in situ* generation of the azirines **1c** and **1d** from the terminal vinyl azides[4]) possessed small vicinal coupling constants of 2.4 and 2.7 Hz, respectively, thus proving the trans arrangement of the aziridine ring protons.

3,3-Dimethyl-2-phenylazirine failed to react with **2** in refluxing toluene. A similar inertness to reaction of this azirine with cyclopentadienones was also observed[2] and explanations were offered[5] to account for this.

In order to have a diagnostic probe for the nmr, most of the subsequent chemical reactions were conducted with the *tert*-butyl adduct **3d**.

B. Oxido Bridge Opening. When the crude reaction mixture containing **3d** was chromatographed over silica gel, a small amount of diol **4** (in addition to pure **3d**) was isolated. This reaction was carried out more efficiently by stirring the adduct **3d** with silica gel in USP-grade ether. An analogous product **5** was also noted from the reaction of **3a** on silica gel. The trans-diol structure assignment is based on the assumption that the more stable trans diol will be formed preferentially and in analogy with hydride opening of the oxido bridge, which is expected to proceed in a trans manner. When crude **3d** was chromatographed on Merck acid-washed alumina, and solvent mixtures containing undistilled ether were used as eluents, two isomers indicating the incorporation of one molecule of water were separated. The minor one, mp 171°, corresponded to **4** while the major component (mp 130°) had similar ir and nmr properties, and has tentatively been assigned the isomeric cis-diol structure **6**.[17]

The utility of this reaction was examined with other nucleophiles such as alkoxide and hydride. By refluxing **3d** in an appropriate alcohol, opening of the oxido bridge occurred regiospecifically with the incorporation of a molecule of solvent to give the adducts **9** and **10**.



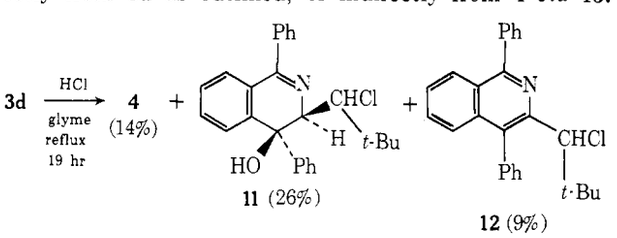
6

7, R = H; $R^1 = t\text{-Bu}$
8, R = Ph; $R^1 = H$
4, R = H; $R^1 = t\text{-Bu}$
5, R = Ph; $R^1 = H$

9, R = Me
10, R = Et

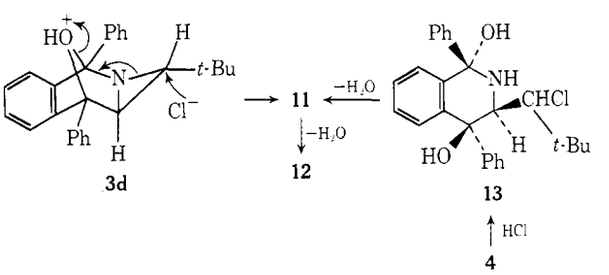
To prove the regiochemistry of opening we selected hydride as the nucleophile. Opening of **3b** by $LiAlH_4$ was postulated[7] to proceed to **8** on the basis of the chemical shift of the benzylic hydrogen. We were able to verify this assignment by the isolation of **7**, from the reduction of **3d**. The singlet (τ 5.63) for the benzylic hydrogen clearly indicated that hydride had entered at the carbon atom of the oxido bridge next to the aziridine ring nitrogen. The regioselective opening of the oxido bridge by H_2O, alkoxide, or hydride vicinally to the aziridine N suggests that the latter is capable of stabilizing adjacent incipient positive charges without undergoing ring opening. Backside trans opening of the oxido bridge is assumed.

Treatment of **3d** with concentrated HCl in refluxing glyme for 19 hr produced three products, **4**, **11**, and **12**, separated by ptlc. The first product **4** corresponded to that isolated from the hydration of **3d** on silica gel. The second product **11**, to which the dihydroisoquinoline structure has been assigned, may have been formed directly from **3d** as outlined, or indirectly from **4** *via* **13**.



11 (26%) **12** (9%)

Opening to a seven-membered ring was ruled out by the nmr spectra. When **4** was treated under the reaction conditions it was smoothly converted to **12**, presumably via **11** which on dehydration yielded **12**. Similarly **11** was converted to **12**.

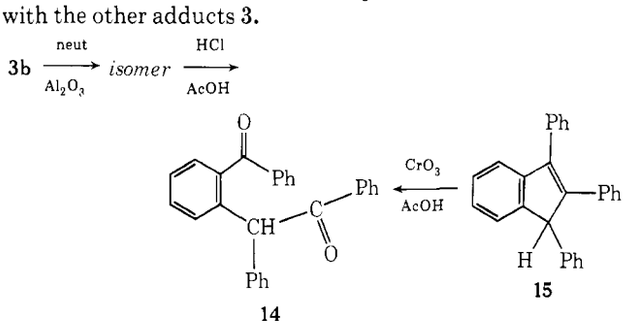


3d **12** **13** **4**

C. Isomerization of Adducts. As mentioned earlier, the adducts **3a-d** were purified by chromatography over Merck acid-washed alumina. We have found that this technique conveniently removes excess azirine from the product and that the azirines are not eluted from the column even when methanol is used as eluent (considerable amount of azirine still contaminated **3a** and **3b** after chromatography on silica gel). However, when the crude reaction mixture containing **3b** was chromatographed over Woelm neutral alumina (activity I) (or the pure adduct **3b** was merely stirred in solution with the chromatographic support) a colorless, crystalline isomer, mp 158°, was obtained very quickly (<1 hr) and in good yield (50-60%). Spectra comparison, chemical conversions, and synthetic schemes discussed below led to the elucidation of its structure as **20b.**

The ir spectrum indicated the absence of the OH, NH, and C=O moieties, while the nmr spectrum clearly indicated the intactness of the -CHMe- unit (three-proton doublet, J = 6.5 Hz) at τ 8.68 and one-proton quartet at τ 6.35. The aromatic region displayed a 17 H multiplet at τ 3.10-2.30 and a low-field 2 H multiplet at τ 2.25-2.00, characteristic of the ortho protons of a benzene ring attached to a C=N, as observed in 3*H*- and 2*H*-azepines.[5]

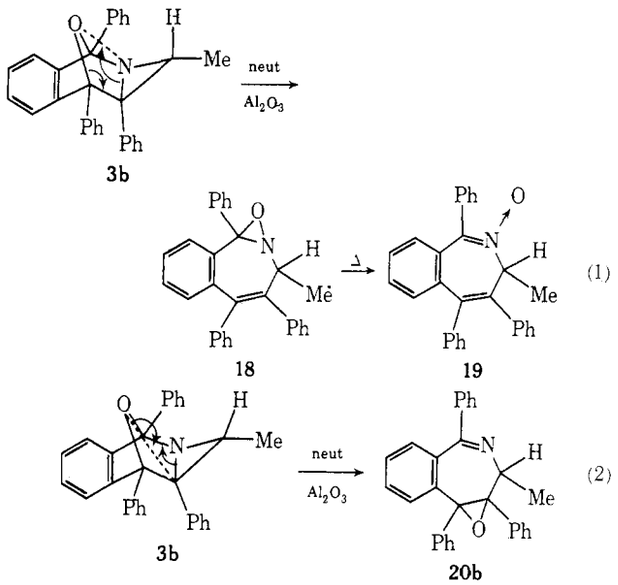
Furthermore, the isomer failed to react with $LiAlH_4$, dilute HCl-methanol reflux, or refluxing KOH-MeOH, and it was unchanged by thermolysis in refluxing xylene. However upon treatment with refluxing glacial acetic acid containing a few drops of concentrated HCl it was converted to the diketone **14** [ν_{max} (KBr) 1672 and 1650 cm^{-1}]. The latter was independently synthesized by the chromic acid oxidation of 1,2,3-triphenylindene (**15**). This degradation gave a clue as to the structure of one side of the molecule, but since the other part (containing the methyl group) had been lost it was necessary to examine whether the same isomerization process can be observed with the other adducts **3.**

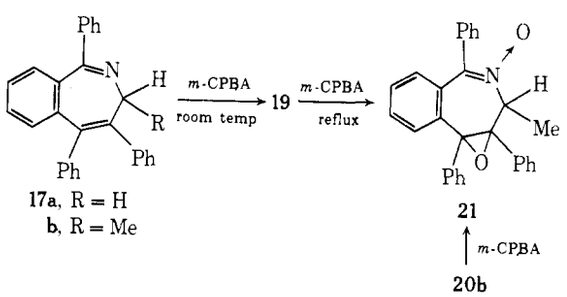


Unfortunately, the isomerizations of **3a, 3c,** and **3d** were neither as clean nor as rapid as with **3b.** However, in analogy with **3b,** they all gave colorless solutions in chloroform or ether which rendered a blue-green fluorescence on treatment with neutral alumina. The *tert*-butyl adduct **3d** showed no rearrangement (by nmr or tlc) after 5 days. However, on exposure of **3a** to neutral alumina, a crystalline isomer (**20a**) was isolated in low yield. Whereas the nmr spectrum of **3a** had shown two singlets at τ ($CDCl_3$) 7.70 and 6.66 for the aziridine ring protons, the isomer displayed two doublets (J = 10.5 Hz, each 1 H) at τ ($CDCl_3$) 6.42 and 5.22. It proved fortunate that this work was conducted concurrent with our study on cyclopentadienones,[2] since it was soon recognized that the nmr spectra of the isomers of **3a** and **3b** were very similar to those of the 2*H*-azepine adducts **17a** and **17b** derived from 1,3-diphenylinden-2-one (**16**) and the azirines **1a** and **1b.**[3,5] For example, **17a** showed two doublets (J = 10 Hz, each 1 H) at τ 6.40 and 5.06; **17b** had a doublet (J = 6.5 Hz, 3 H) at τ 8.55 and a quartet (1 H) at τ 6.40.

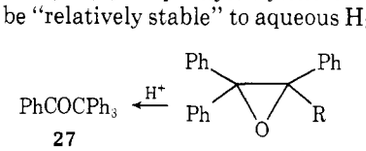
Two structures, the *N*-oxide **19** arising *via* **18** or the epoxide **20** formed by direct rearrangement of **3** (see Scheme I), would fit all the data described. In fact **19,** conveniently prepared as colorless crystals, mp 218°, from the 2*H*-azepine **17b,** possessed different physical and chemical properties than those of the isomer of **3b.** This excluded path 1. A direct synthesis of **20b** (path 2) from **17b** was not possible; however, when the 2*H*-azepine **17b** was heated in $CHCl_3$ with excess *m*-chloroperbenzoic acid (*m*-CPBA) it was slowly converted to the epoxide **21** (*via* **19**).

Scheme I

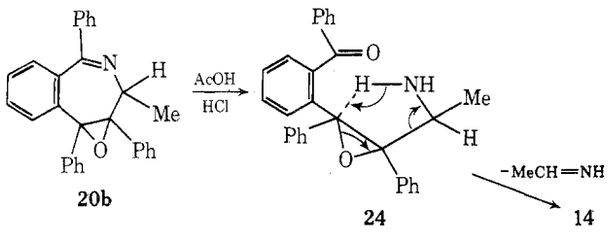




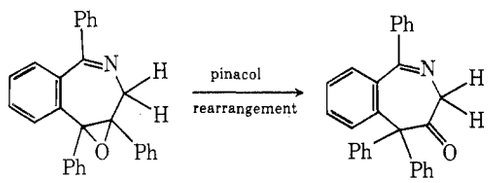
When the isomer of **3b** was treated with *m*-CPBA in chloroform at 25° it was converted to the same *N*-oxide **21.** It was therefore concluded that the isomerization of the adducts **3a** and **3b** on neutral alumina affords the epoxy-2*H*-azepines **20a** and **20b.** Scheme I (path 2) points out again the ability of the aziridine N to participate in the opening of the oxido bridge. The inertness of **20b** to acid, base, and $LiAlH_4$ may be compared to the resistance of tetraphenylethylene oxide (**22**) to these three reagents.[8] Similarly, 1-methyl-1,2,2-triphenylethylene oxide (**23**) was reported[19] to be "relatively stable" to aqueous H_2SO_4.

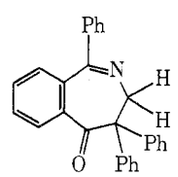


Several processes may be postulated to account for the production of the diketone **14** on AcOH-HCl hydrolysis of **20b,** one of which is shown. It involves initial hydrolysis of the C=N bond to afford **24,** which then undergoes a hydrogen transfer with elimination of acetaldehyde imine to give **14.**



When the crude adduct **3a** was adsorbed in a column of neutral alumina and allowed to stand overnight, elution the following day produced a small amount of the epoxide **20a.** However, the major product isolated turned out to be yet another isomer of **3a.** This material was obtained as colorless crystals, mp 176°, τ ($CDCl_3$) 5.23 (s, 2 H), 3.20–2.40 (m, 19 H). This isomer has been assigned the cyclic ketone structure **25,** rather than the regioisomer **26,** on the





basis of its ir adsorption (1710 cm^{-1}). Both may be interpreted as being formed *via* a pinacol-type rearrangement of **3a.**[20] Similar rearrangements have been observed in other epoxides,[18a] for example **22** → **27,** and in adducts of 1,3-diphenylisobenzofuran (**2**) with cyclopropenes,[11] although in this latter case the opposite regioisomer was formed. The appearance of the methylene ring protons of **25** as a singlet in the nmr spectrum showed that ring inversion was fairly rapid on the nmr time scale when compared to the epoxy compound **20a** and the 2*H*-azepine **17a.**

Experimental Section[21]

Reaction of 2-Phenyl-1-azirine (1a) with 1,3-Diphenylisobenzofuran (2). Adduct 3a. α-Azidostyrene (2.0 g, 13.8 mmol) was converted to **1a** by heating[22] under reflux in toluene (25 ml) for 2 hr, at which time gas evolution had ceased, and the furan (2.70 g, 10 mmol) was added. The mixture was refluxed for an additional 17 hr until the blue-green fluorescence due to **2** disappeared. The solvent was removed to yield an orange oil, which was chromatographed over Merck acid-washed alumina. Ether–hexane (1:2) eluted a colorless foam (3.60 g, 93%). Trituration in hexane with cooling gave a white solid. Recrystallization from hexane gave the exo adduct **3a** (3.25 g, 84%) as colorless crystals: mp 94°; nmr ($CDCl_3$) τ 7.70 (s, 1 H), 6.66 (s, 1 H), 3.40–3.10 (m, 2 H), 3.00–1.90 (m, 17 H); ν_{max} (KBr) 1451, 1311, 1020, 1007, 995, 769 (s), and 710 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 387 (17), 386 (13), 359 (17), 285 (13), 284 (54), 282 (20), 271 (77), 270 (100), 252 (10), 241 (39), 239 (17), 206 (14), 173 (16), 165 (21), 117 (20), 105 (18), 103 (11), 77 (22).

Anal. Calcd for $C_{28}H_{21}NO$: C, 86.8; H, 5.5. Found: C, 86.6; H, 5.4.

Reaction of 3-Methyl-2-phenyl-1-azirine (1b) with 2. Adduct 3b. The furan and the azirine[22] were refluxed in toluene for 24 hr as for **3a.** Chromatography and elution with hexane–ether (3:1) gave a colorless foam (3.70 g, 92%), which on cooling and trituration with hexane gave large, colorless crystals (3.60 g, 90%). Recrystallization from hexane produced the pure exo adduct **3b** as colorless crystals: mp 110° (lit.[7] mp 192–194°);[8] nmr ($CDCl_3$) τ 8.95 (d, J = 6.0 Hz, 3 H), 6.48 (q, J = 6.0 Hz, 1 H), 3.55–3.20 (m, 2 H), 3.10–1.90 (m, 17 H); ν_{max} (KBr) 1450, 1312, 1021, 760 (s), and 710 cm^{-1}; mass spectrum *m/e* (rel intensity) 401 (14), 359 (8), 296 (12), 283 (9), 271 (23), 270 (100), 241 (12), 239 (7), 165 (8), 131 (36), 130 (10), 115 (5), 105 (6), 104 (6), 103 (9), 77 (11).

Anal. Calcd for $C_{29}H_{23}NO$: C, 86.75; H, 5.8. Found: C, 86.9; H, 5.9.

Reaction of 3-Phenyl-1-azirine (1c) with 2. Adduct 3c. The furan (1.0 g, 3.72 mmol) and *trans*-β-azidostyrene[23] (0.90 g, 6.19 mmol) were heated in toluene (15 ml) for 1.5 hr. Work-up as described for **3a** gave 1.2 g of **3c,** and after recrystallization 0.94 g (65%) as colorless granules: mp 145°; nmr ($CDCl_3$) τ 7.16 (d, J = 2.4 Hz, 1 H), 6.07 (d, J = 2.4 Hz, 1 H), 2.95–2.00 (m, 19 H); ν_{max} (KBr) 1454, 1316, 990, 756, and 707 cm^{-1}; mass spectrum *m/e* (rel intensity) 387 (21), 384 (24), 283 (100), 282 (33), 271 (14), 270 (51), 241 (13), 178 (10), 165 (14), 105 (26), 77 (27).

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

Reaction of 3-*tert*-Butyl-1-azirine (1d) with 2. Adduct 3d. *trans*-1-Azido-3,3-dimethylbut-1-ene[22] (2.1 g, 16.8 mmol) and the furan (2.7 g, 10 mmol) heated in toluene (15 ml) for 16 hr and worked up as above produced **3d** as a white solid (3.01 g, 82%), recrystallized from hexane: colorless needles, mp 104°; nmr ($CDCl_3$) τ 9.04 (s, 9 H), 7.40 (d, J = 2.7 Hz, 1 H), 7.25 (d, J = 2.7 Hz, 1 H), 3.00–2.70 (m, 4 H), 2.60–1.90 (m, 10 H); ν_{max} (KBr) 1450, 1313, 987, 763, 751, and 707 cm^{-1}; mass spectrum *m/e* (rel intensity) 367 (7), 284 (24), 283 (100), 282 (5), 271 (8), 270 (28), 241 (7), 239 (5), 165 (7), 105 (8), 77 (5); m* 218.5 is 367 → 283.

Anal. Calcd for $C_{26}H_{25}NO$: C, 85.0; H, 6.9. Found: C, 85.0; H, 6.95.

Hydration of the *tert*-Butyl Adduct 3d on Silica Gel. The adduct **3d** (510 mg) was stirred in USP-grade ether (40 ml) in the presence of Fisher silica gel (10 g, 28–200 mesh) for 21 hr, after which time the silica was filtered and washed with anhydrous ether (50 ml). Removal of the solvent gave a foam (510 mg, 95%) which rapidly solidified on trituration with hexane. Recrystallization from hexane gave the pure trans diol **4** (373 mg, 70%) as colorless crystals: mp 171°; nmr ($CDCl_3$) τ 9.04 (s, 9 H), 7.55–7.25 (br, 2 H), 2.85–2.10 (m, 14 H); addition of D_2O resolved the broad adsorption at τ 7.55–7.25 into two sharp doublets (J = 3.8 Hz, each 1 H) at τ 7.46 and 7.36; ν_{max} (KBr) 3400–2700 (br d), 1460, 1450 (sh), 1210, 1065, 1058, 973, 948, 922, 767, and 710 cm^{-1}; mass spectrum *m/e* 385, 367, 328, 287, 283 (100), 270, 235, 209, 105; m* 252 is 328 → 287, m* 218.5 is 367 → 283.

Anal. Calcd for $C_{26}H_{27}NO_2$: C, 81.0; H, 7.1. Found: C, 80.8; H, 7.1.

Hydration of the *tert*-Butyl Adduct 3d on Acid-Washed Alumina. The crude reaction mixture containing **3d** [formed from the furan **2** (1.0 g, 3.7 mmol) and the vinyl azide (2.0 g, 16 mmol) in refluxing toluene (15 ml) for 5 hr] was chromatographed over Merck acid-washed alumina. Ether–hexane (1:4) eluted the exo adduct **3d** (700 mg, 51%). Increasing amounts of ether (up to 100%) eluted an oil (712 mg) from which the trans diol **4** separated (47 mg, 3%). The residual oil was subjected to ptlc and the fastest running component was removed, giving a colorless solid (222 mg, 16%). Recrystallization from hexane yielded colorless crystals of the cis diol **6:** mp 130°; nmr ($CDCl_3$) τ 9.00 (s, 9 H), 7.95 (br d, 1 H), 7.32 (br d, 1 H), 2.85–2.05 (m, 14 H); addition of D_2O resolved the two broad doublets (J = 3.4 Hz); ν_{max} (KBr) 3500–3000 (br), 1462, 1210, 1202, 1049, 910, 775, 761, and 707 cm^{-1}; mass spectrum *m/e* 385, 367, 328, 310, 300, 287, 283 (100%), 270, 241, 235, 209, 195, 178, 165, 152, 105, 99; m* 350 is 385 → 367, m* 218.5 is 367 → 283.

Anal. Calcd for $C_{26}H_{27}NO_2$: C, 81.0; H, 7.1; N, 3.6. Found: C, 81.2; H, 7.2; N, 3.7.

Reaction of the *tert*-Butyl Adduct 3d with Methanol. The adduct **3d** (200 mg) was heated under reflux in absolute methanol (15 ml) for 24 hr. Removal of the solvent and crystallization of the residue from hexane yielded the trans methoxy alcohol **9** (84 mg, 39%) as colorless crystals: mp 118°; nmr ($CDCl_3$) τ 9.01 (s, 9 H), 7.68 (br d, J = 3.0 Hz, 1 H), 7.48 (br d, J = 3.0 Hz, 1 H), 6.66 (s, 3 H), 2.80–2.20 (m, 14 H); addition of D_2O resolved the two broad doublets; ν_{max} (KBr) 3285, 1450, 1076, 990 (s), 763, and 709 cm^{-1}; mass spectrum *m/e* 399, 367, 310, 300, 283 (100%), 270, 241, 193, 178, 165, 105, 77; m* 218.5 is 367 → 283.

Anal. Calcd for $C_{27}H_{29}NO_2$: C, 81.2; H, 7.3. Found: C, 81.2; H, 7.4.

Reaction of the *tert*-Butyl Adduct 3d with Ethanol. The adduct **3d** (700 mg) heated in ethanol (25 ml) for 2 hr afforded 573 mg (72%) of the trans ethoxy alcohol **10:** mp 145°; nmr ($CDCl_3$) τ 9.00 (s, 9 H), 8.85 (t, J = 7 Hz, 3 H), 9.20–8.50 (v br, 1 H), 7.80–7.40 (v br, 2 H), 6.70–6.15 (2 q, AB, J = 7.0 and 2.5 Hz, 2 H),

2.85–2.20 (m, 14 H); upon addition of D_2O the broad signal at τ 9.20–8.50 disappears and the broad signal at τ 7.80–7.40 is resolved into two doublets (J = 3.0 Hz, each 1 H) at τ 7.66 and 7.51; ν_{max} (KBr) 3275, 1076, 994, 882, 768, and 711 cm^{-1}; mass spectrum m/e 413, 384, 367, 315, 287, 283 (100%), 270, 241, 209, 193, 178, 165, 105; m* 269.5 is 367 → 315, m* 261.5 is 315 → 287, m* 252 is 287 → 270, m* 218.5 is 367 → 283.

Anal. Calcd for $C_{28}H_{31}NO_2$: C, 81.3; H, 7.6; N, 3.4. Found C, 81.5; H, 7.7; N, 3.5.

Reduction of the *tert*-Butyl Adduct 3d with $LiAlH_4$. The adduct **3d** (256 mg, 0.7 mmol) was heated under reflux for 24 hr in tetrahydrofuran (15 ml) containing $LiAlH_4$ (40 mg, 1.05 mmol). An aqueous work-up provided a colorless foam (200 mg, 78%) which on extended trituration and cooling to −78° produced crystals. Recrystallization from hexane yielded the pure aziridino alcohol **7** as colorless crystals: mp 66°; nmr ($CDCl_3$) τ 9.00 (s, 9 H), 8.39 (d, J = 3.0 Hz, 1 H), 7.90 (s, 1 H, OH), 7.14 (d, J = 3.0 Hz, 1 H), 5.63 (s, 1 H), 3.00–2.45 (m, 13 H), 2.20–1.95 (m, 1 H); ν_{max} (KBr) 3450 (br), 1491, 1450, 1011, 768, 740, and 707 cm^{-1}; mass spectrum m/e (rel intensity) 369 (48), 352 (13), 326 (25), 312 (10), 285 (24), 284 (100), 283 (13), 271 (11), 201 (24), 206 (36), 193 (16), 179 (16), 178 (16), 165 (11), 105 (13), 86 (61), 71 (29).

Anal. Calcd for $C_{26}H_{27}NO$: C, 84.5; H, 7.4. Found: C, 84.5; H, 7.5.

Treatment of the *tert*-Butyl Adduct 3d with HCl. A. The aziridine **3d** (200 mg, 0.545 mmol) was heated under reflux for 19 hr in glyme (5 ml) containing 3 drops of concentrated HCl. The solvent was removed and the yellow-green foam was extracted with chloroform–water. The organic layer was washed with dilute Na_2CO_3 solution and dried over $MgSO_4$ to give a yellow foam (159 mg). The foam was applied to a silica gel preparative plate (20 × 20 × 0.2 cm) and eluted with ether–hexane (1:1). Three bands were extracted with ether; the slowest (30 mg, 14%) was shown to be the trans diol **4**, mp 171°. The center band provided colorless crystals (59 mg, 26%) from hexane of **3-chloroneopentyl-4-hydroxy-1,4-diphenylisoquinoline (11):** mp 163°; nmr ($CDCl_3$) τ 8.80 (s, 9 H), 6.30 (v br, -OH), 5.95 (d, J = 5.3 Hz, 1 H), 5.07 (d, J = 5.3 Hz, 1 H), 2.80–2.20 (m, 14 H); ν_{max} (KBr) 3580 (w), 1606, 1446, 1327, 1320, 1164, 963, 797, 777, 764, and 710 cm^{-1}; mass spectrum m/e (rel intensity) 403 (1), 388 (2), 369 (14), 368 (48), 352 (2), 346 (3), 310 (5), 271 (23), 270 (100), 241 (9), 193 (5), 165 (7), 105 (8); characteristic ^{35}Cl and ^{37}Cl pattern for m/e 403, 388, 346, and 310 peaks.

Anal. Calcd for $C_{26}H_{26}NOCl$: C, 77.2; H, 6.5. Found: C, 77.3; H, 6.5.

The fastest component (21 mg, 9%) afforded colorless crystals from hexane of **3-chloroneopentyl-1,4-diphenylisoquinoline (12):** mp 182°; nmr ($CDCl_3$) τ 8.87 (s, 9 H), 5.10 (s, 1 H), 2.75–1.60 (m, 14 H); ν_{max} (KBr) 1385, 777, 756, and 710 cm^{-1}; mass spectrum m/e (rel intensity) 385 (6), 350 (7), 335 (5), 334 (10), 332 (7), 331 (26), 330 (23), 329 (100), 328 (22), 296 (14), 295 (57), 294 (47), 293 (45), 292 (45), 291 (22), 290 (10), 258 (6), 71 (10); m* 261 is 329 → 293; ^{35}Cl and ^{37}Cl patterns for m/e 385, 370, and 329 peaks.

Anal. Calcd for $C_{26}H_{24}NCl$: C, 81.0; H, 6.3. Found: C, 81.1; H, 6.4.

B. When the reaction was allowed to proceed for 68 hr before work-up, the isoquinoline **12** was isolated (85%) directly. Neither the trans diol **4** nor the dihydroisoquinoline **11** was detected by tlc or nmr after 68 hr at reflux.

Reaction of the Trans-Diol 4 with HCl. The diol **4** (205 mg, 0.53 mmol) was heated under reflux in glyme (5 ml) containing 6 drops of concentrated HCl for 22 hr. Removal of the solvent gave a yellow solid, which was dissolved in chloroform and washed with dilute Na_2CO_3 solution. The organic layer was dried with $MgSO_4$ and the solvent was removed to afford a yellow oil (200 mg) which rapidly solidified. (Nmr analysis of this solid showed it to be at least 90% pure isoquinoline **12.**) Recrystallization from hexane gave the pure isoquinoline **12**, mp 182°.

Hydration of 3a on Silica Gel. α-Azidostyrene (1.5 g, 10.3 mmol) was heated under reflux for 2 hr in toluene. The furan (2.0 g, 7.4 mmol) was added and the mixture was refluxed for an additional 23 hr. The solvent was removed and the oil was chromatographed on silica gel. Ether–hexane (1:4) eluted the adduct **3a** (900 mg) contaminated with a small amount of azirine **1a.** Increasing amounts of ether (USP grade) eluted a foam (1.9 g) which was mainly **3a.** However, the later fractions crystallized on trituration with hexane. In this manner there was obtained a sand-like material (400 mg). Recrystallization (with charcoal) from chloroform–hexane gave colorless needles (286 mg, 10%) of the trans diol **5:** mp 186°; nmr ($CDCl_3$) τ 9.30–8.55 (v br, 1 H), 7.85 (br s, 1 H), 6.93 (br s, 1 H), 3.30–2.92 (m, 3 H), 2.92–2.16 (m, 16 H); the high-field signal τ 9.30–8.55 disappears with D_2O and the two broad singlets become sharp; ν_{max} (KBr) 3320, 1450, 1211, 1061, 993, 969, 946, 791, 779, 766, 710, and 625 cm^{-1}; mass spectrum m/e 405, 387, 386, 359, 284, 282, 271, 270, 252, 241, 239, 209, 206, 193, 178, 165, 152, 135, 119, 117, 105, 91, 77.

Anal. Calcd for $C_{28}H_{23}NO_2$: C, 82.9; H, 5.7; N, 3.5. Found: C, 82.8; H, 5.8; N, 3.5.

Isomerization of the Adduct 3b to 20b with Neutral Alumina. A. The reaction mixture containing crude **3b** [formed from the azirine **1b** (500 mg, 3.8 mmol) and the furan **2** (950 mg, 3.5 mmol) in refluxing toluene (15 ml) for 24 hr] was chromatographed over Woelm neutral alumina (activity I). Upon absorption, the chromatographic support acquired a brilliant green-blue fluorescence. Elution with benzene caused the fluorescent material to move down the column. There was obtained a blue-green fluorescent oil which rapidly solidified (600 mg, 81%). Recrystallization from hexane gave colorless crystals of **3,4-epoxy-2-methyl-3,4,7-triphenylbenz[*e*]-2*H*-azepine (20b):** mp 158°; nmr ($CDCl_3$) τ 8.68 (d, J = 6.5 Hz, 3 H), 6.35 (q, J = 6.5 Hz, 1 H), 3.10–2.30 (m, 17 H), 2.25–2.00 (m, 2 H); ν_{max} (KBr) 1594, 1567, 1448, 1295, 960, 767, and 700 cm^{-1}; mass spectrum m/e 401, 359, 296, 286, 283, 275, 252, 209, 165, 152, 131, 105, 77.

Anal. Calcd for $C_{29}H_{23}NO$: C, 86.75; H, 5.8; N, 3.5. Found: C, 86.8; H, 5.8; N, 3.4.

B. The pure aziridine **3b** (211 mg) was stirred at 25° in benzene (20 ml) containing Woelm neutral alumina (10 g, activity I). The mixture rapidly acquired a blue-green fluorescence. After 2 hr the color had faded. The mixture was filtered to yield (after recrystallization from hexane) the epoxy-2*H*-azepine **20b** (115 mg, 55%). The time required for completion of this isomerization was variable (1–50 hr) depending upon the alumina and the solvent.

Reaction of the Epoxy-2*H*-azepine 20b with Concentrated HCl–Acetic Acid. The epoxide **20b** (126 mg, 0.315 mmol) was heated under reflux for 4 hr in glacial acetic acid (2.5 ml) containing 2 drops of concentrated HCl. The solvent was removed to give an orange oil, which was taken up in chloroform, washed with dilute Na_2CO_3 solution, and dried over $MgSO_4$. There was obtained a fluorescent yellow-green gum (95 mg) which slowly solidified. Recrystallization from hexane yielded **1-(*o*-benzoylphenyl)-1-phenylacetophenone (14)** as colorless crystals: mp 91°; nmr ($CDCl_3$) τ 3.33 (s, 1 H), 2.80–1.85 (m, 19 H); ν_{max} (KBr) 1672, 165 1274, 1223, 937, and 707 cm^{-1}; mass spectrum m/e 376, 271, 255, 254, 241, 194, 165, 105, 93, 86, 77.

Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.1; H, 5.4. Found: C, 85.9; H, 5.4.

Oxidation of 1,2,3-Triphenylindene (15).[24] The indene (500 mg, 1.45 mmol) and chromium trioxide (450 mg, 4.5 mmol) were stirred in glacial acetic acid (15 ml) at 50–70° for 15 min, at which time the hot mixture was poured into ice water (50 ml). Extraction with ether, followed by washing with water and dilute NaOH solution, gave a brown oil (450 mg). This was applied to a preparative tlc plate (silica, 20 × 20 × 0.2 cm) and eluted with ether–hexane (3:7). The faster band afforded the diketone **14** (100 mg, 18%), mp 91°. The slower band yielded 1,2-dibenzoylbenzene (133 mg, 22%).

Isomerization of 3a to 20a on Neutral Alumina. The furan **2** (1.0 g, 3.7 mmol) and the azirine **1a** (0.7 g, 6.0 mmol) were heated under reflux in toluene (12 ml) for 24 hr. The solvent was removed and the crude adduct **3a** was dissolved in chlorform. The solution was added to a dry column of Woelm neutral alumina (activity I) and the column was allowed to stand for 20 hr before eluting. The adsorbed material turned orange. Elution with ether afforded the furan **2** (100 mg, 10%) closely followed by a colorless oil (200 mg, 14%) which soon solidified. Recrystallization gave pure **3,4-epoxy-3,4,7-triphenylbenz[*e*]-2*H*-azepine (20a)** as colorless prisms from hexane: mp 152°; nmr ($CDCl_3$) τ 6.42 (d, J = 10.5 Hz, 1 H), 5.22 (d, J = 10.5 Hz, 1 H), 3.00–1.90 (m, 19 H); ν_{max} (KBr) 1600, 1447, 1309, 946, 770, and 705 cm^{-1}; mass spectrum m/e (rel intensity) 387 (17), 285 (22), 284 (100), 282 (21), 270 (29), 252 (12), 207 (38), 206 (57), 193 (22), 178 (14), 105 (14).

Anal. Calcd for $C_{28}H_{21}NO$: C, 86.8; H, 5.5. Found: C, 87.0; H, 5.6.

Methanol eluted an amorphous orange solid (900 mg). Attempted purification by recrystallization (with charcoal) from methanol gave orange, leafy needles (36 mg), mp 165°. An analytical sample was prepared by ptlc and provided **4,4,7-triphenylbenz[*e*]-2*H*-azepin-3-one (25)** as cream needles: mp 176°; nmr ($CDCl_3$) τ 5.23 (s, 2 H), 3.20–2.40 (m, 19 H); ν_{max} (KBr) 1710, 770, and 704 cm^{-1}; mass spectrum m/e (rel intensity) 388 (10), 387 (33), 360 (12), 359 (56), 358 (100), 282 (7), 281 (13), 280 (6), 268 (8), 253 (6), 252 (9), 118 (5), 75 (8).

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.**

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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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Stevens Rearrangement of Carbamoylaminimides

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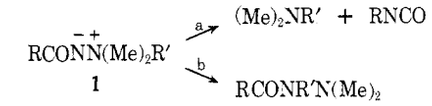
Carbamoylaminimides (**7**) with 1-allyl and 1-benzyl substituents undergo thermal Stevens rearrangements to give semicarbazides (**8**). Thermolysis of 1-(3-methyl-2-butenyl)- and 1-(2-butenyl)aminimides (**9** and **11**) give products resulting from allyl retention, thus ruling out a concerted mechanism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