

Registry No.—1, 33420-45-0; 2, 33420-37-0; 3, 43193-60-8; 4, 22051-80-5; 5, 36023-58-2; 6, 50921-36-3; 7, 36023-60-6; 8, 36023-59-3; 9, 36086-83-6; 11, 36023-63-9; 12, 36023-62-8; 13, 41245-87-8; DISN, 28321-79-1; DAMN, 1187-42-4.

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## Synthesis of Adamantane Derivatives. XXV.<sup>1</sup> Synthesis and Reactions of 1- and 2-Adamantyl Isocyanides

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1- (4) and 2-adamantyl isocyanide (11) were prepared by the reactions of the corresponding amines with dichlorocarbene using a phase-transfer method and/or by dehydration of *N*-1-adamantylformamide. 4 was very stable in the atmosphere while 11 was converted rapidly to *N*-2-adamantylformamide (13) by the atmospheric moisture. Some simple derivatives of 4 and 11 such as 1-(1-adamantyl)- (5) and 1-(2-adamantyl)tetrazole (12), 1-(1-adamantyl)-2,4-dithioxo-1,2,3,4-tetrahydrotriazine (6), and *N*-adamantyl-*N'*-pentamethyleneformamidine (7) were prepared. Thermal rearrangements of 4 and 11 to the corresponding nitriles 8 and 14 were compared with that of *tert*-butyl isocyanide. The relative rate of the rearrangement for gas phase at 200° was 1.0:0.22:0.24 for *t*-BuNC, 4, and 11. The rate of the rearrangement of 4 in diglyme at 200° was 11 times faster than that of 11 and the formation of considerable amounts of adamantane was observed.

Adamantyl isocyanides have not been described in the extensive literature on adamantane chemistry.<sup>2,3</sup> This paper describes the facile preparation of 1- and 2-adamantyl isocyanides and some of their fundamental chemical and thermal behaviors.

### Results and Discussion

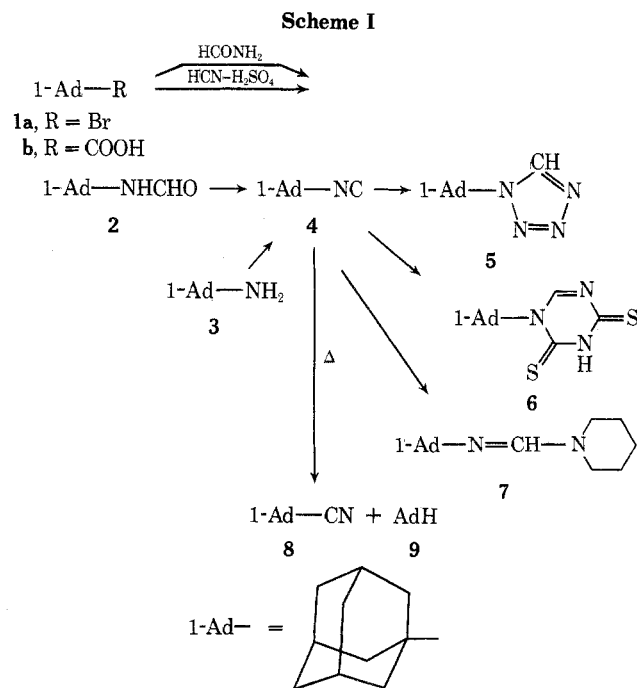
**Preparation and Properties of 1- and 2-Adamantyl Isocyanides.** 1-Adamantyl isocyanide (4) was prepared in 61% yield by dehydration with triphenylphosphine-carbon tetrachloride-triethylamine<sup>4</sup> of *N*-1-adamantylformamide (2), which was obtained by the Ritter reaction on 1-adamantanecarboxylic acid (1b)<sup>5</sup> or 1-adamantyl bromide (1a), and/or by heating 1a in formamide. It was also prepared by the Hofmann carbylamine reaction of 1-adamantanamine (3) in 40% yield by using a 3-molar excess of dichlorocarbene, which was generated from CHCl<sub>3</sub> and *t*-BuOK in *n*-hexane.<sup>6</sup> The yield of 4 was improved up to 54% in the carbylamine reaction by using benzyltriethylammonium chloride, a phase-transfer catalyst.<sup>7,8</sup> 1-Adamantyl isocyanide (4) formed colorless crystals, mp 185–186°, and had no foul odor but a rather fragrant one. The structure was indicated by ir (KBr) absorption at 2150 cm<sup>-1</sup> ( $\nu_{N=C}$ ), mass spectral ion peaks at *m/e* (rel intensity) 161 (M<sup>+</sup>, 5), 135 (95), and 41 (100), and nmr (CDCl<sub>3</sub>) signals at  $\delta$  3.30–1.85 (broad s, 9 H) and 1.80–1.56 (unsymmetrical s, 6 H).

2-Adamantyl isocyanide (11) was prepared by the carbylamine reaction of 2-adamantanamine (10). *N*-2-Adamantylformamide (13) was not chosen as the starting material because it was not obtained by the conventional formylation of 10 with formic acid. The yield of 11 in the carbylamine reaction was raised from 40% to 76% by application of the phase-transfer technique<sup>7</sup> (50% aqueous KOH-C<sub>6</sub>H<sub>6</sub>-benzyltriethylammonium chloride). Colorless crystals of 11 were obtained, mp 186–188°, having a similar odor to 4 and ir (KBr) absorption at 2140 cm<sup>-1</sup> ( $\nu_{N=C}$ ),

mass spectral ion peaks at *m/e* (rel intensity) 161 (M<sup>+</sup>, 34), 135 (94), and 106 (100), and nmr (CDCl<sub>3</sub>) signals at  $\delta$  3.41 (broad s, 1 H) and 2.35–1.30 (m, 14 H).

The 1 isomer 4 was very stable and was largely recovered even after stirring in CHCl<sub>3</sub>-H<sub>2</sub>O in the presence of a catalytic amount of sulfuric acid for 3 days at room temperature. In contrast the 2 isomer 11 was very sensitive to atmospheric moisture and was converted rapidly to formamide 13.

Both 4 and 11 afforded the corresponding 1-substituted tetrazole derivatives 5 and 12 in 92 and 54% yields, re-



**Table I**  
Thermal Rearrangement Products of 4 and 11 at 200°

| Isocyanide                  | Solvent           | Reaction time, hr | Recovered isocyanide, % <sup>a</sup> | Product, % <sup>a</sup> |            |                     |
|-----------------------------|-------------------|-------------------|--------------------------------------|-------------------------|------------|---------------------|
|                             |                   |                   |                                      | Nitrile                 | Adamantane | Others <sup>b</sup> |
| 4                           | None <sup>c</sup> | 4.0               | 61                                   | 35                      | Trace      | 4                   |
| 4                           | Diglyme           | 1.5               | 4                                    | 56                      | 40         | Trace               |
| 11                          | None <sup>c</sup> | 4.0               | 40                                   | 28                      | 1          | 31 <sup>d</sup>     |
| 11                          | Diglyme           | 2.0               | 70                                   | 20                      | 8          | 2                   |
| <i>t</i> -BuNC <sup>e</sup> | None <sup>c</sup> | 1.5               | 55                                   | 45                      |            |                     |

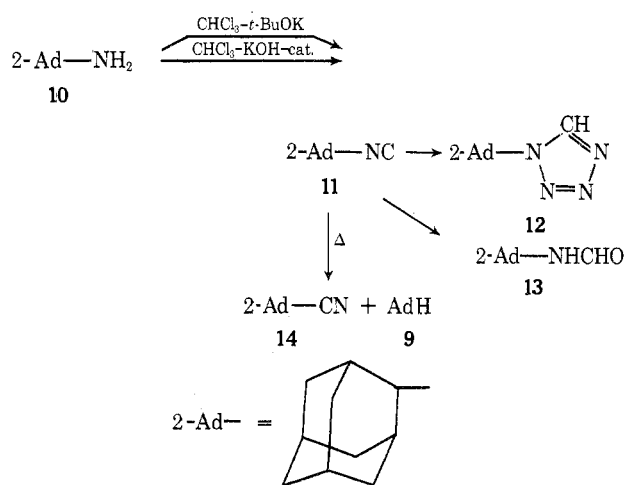
<sup>a</sup> Glpc analysis. <sup>b</sup> Unidentified. <sup>c</sup> In a sealed tube at *ca.* 30 mm. <sup>d</sup> This was largely adamantan-2-one and decreased to 4–6% in argon atmosphere. <sup>e</sup> *Cf.* ref 13.

**Table II**  
First-Order Rate Constants of Thermal Rearrangement of 4, 11, and *t*-BuNC

| Isocyanide                  | Solvent           | Temp, °C | $k_1 \times 10^6$ , sec <sup>-1</sup> | $k_1^{rel}$ at 200° | $E_a$ , kcal/mol | Log <i>A</i> | $\Delta S^\ddagger$ , eu/mol |
|-----------------------------|-------------------|----------|---------------------------------------|---------------------|------------------|--------------|------------------------------|
| <i>t</i> -BuNC <sup>a</sup> | None <sup>b</sup> | 200      | 11.2                                  | 1.0                 | 32.0             | 10.83        | -9.9                         |
|                             |                   | 180      | 2.50                                  |                     |                  |              |                              |
| 4                           | None <sup>b</sup> | 200      | 2.42                                  | 0.22                | 26.8             | 7.766        | -23.9                        |
|                             |                   | 180      | 0.695                                 |                     |                  |              |                              |
|                             | Diglyme           | 200      | 50.6                                  | 4.52                | 17.3             | 4.697        | -38.0                        |
|                             |                   | 180      | 22.5                                  |                     |                  |              |                              |
| 11                          | None <sup>b</sup> | 170      | 16.4                                  |                     |                  |              |                              |
|                             |                   | 200      | 2.68 <sup>d</sup>                     | 0.24                |                  |              |                              |
|                             |                   | 200      | 4.60                                  | 0.41                |                  |              |                              |

<sup>a</sup> *Cf.* ref 13. <sup>b</sup> In a sealed tube at *ca.* 30 mm. <sup>c</sup> Temperature accuracy and constancy were within  $\pm 0.7^\circ$ . <sup>d</sup> An approximate value because of extensive side reactions.

**Scheme II**



spectively, on treatment with hydrazoic acid in dry chloroform.<sup>9</sup> The 2,4-dithioxo-1,2,3,4-tetrahydrotriazine derivative 6 was obtained in 85% yield on treatment of 4 with thiocyanic acid, and 4 was converted to *N*-1-adamantyl-*N'*-pentamethyleneformamide (7) in 30% yield by refluxing with piperidine in the presence of cuprous chloride.<sup>10</sup> These conversions are summarized in Schemes I and II.

**Thermal Rearrangement of 4 and 11.** Although the thermal rearrangement of isocyanides to cyanides has long been known, only relatively recently was the reaction shown to proceed *via* a true unimolecular process with the stereochemical integrity maintained at the migrating carbon atom.<sup>11–13</sup> The rearrangement has also been studied theoretically by the "extended Hückel"<sup>14</sup> and the MINDO/2 methods<sup>15</sup> for methyl isocyanide. The first method suggests that the reaction path for a methyl group is an approximate semicircle around the center of the CN bond, with the CN bond lengthening and the methyl group flattening as it shifts, always keeping the same face toward CN. The second method predicts that the rearrangement involves a stable triangular intermediate with

the properties of a  $\pi$  complex rather than an ion pair. The relative rates of the rearrangement of methyl, ethyl, isopropyl, isobutyl, and *tert*-butyl isocyanides are shown to be 5.6:7.8:2.6:2.6:1.0 by Casanova, *et al.*<sup>13</sup> This sequence is in accordance with that expected for an entropy-controlled rather than for an enthalpy-controlled reaction, except for the methyl substituent. In view of the above features of the isocyanide-cyanide rearrangement, it would be of interest to compare the thermal behavior of 4 and 11 with those of simple alkyl isocyanides.

The rearrangement of 4 proceeded smoothly on heating at 200° under reduced pressure (*ca.* 30 mm), affording the nitrile 8.<sup>16</sup> However, that of 11 to nitrile 14<sup>17</sup> was contaminated with considerable amounts of adamantan-2-one as a by-product.<sup>18</sup> In diglyme, considerable amounts of adamantane were produced as a by-product from both 4 and 11. However, no trace of protoadamantane and 4-protoadamantane<sup>2a</sup> was produced from 11. These data are summarized in Table I. The rearrangement was followed by glpc periodically at 200 and 180°, and the observed rate constants for 4, 11, and *t*-BuNC<sup>19</sup> are summarized in Table II. From an Arrhenius plot of  $\log k$  vs.  $1/T$ , activation parameters for the rearrangement were calculated and the results are shown also in Table II.

The fact that 4 rearranges slower than *t*-BuNC might imply that the reaction is actually entropy controlled, as postulated by Casanova, *et al.*,<sup>13</sup> which is supported by the larger negative entropy of activation for 4 than for *t*-BuNC. Furthermore, the only slightly faster rearrangement of *t*-BuNC compared to 4 contrasts with the 10<sup>3</sup> faster solvolysis rate of *tert*-butyl than of 1-adamantyl derivatives, in which the relative reactivity is dependent on the ready formation of cations.<sup>20</sup> Therefore, the isocyanide-cyanide rearrangement should be regarded as a process proceeding *via* an almost neutral intermediate; *i.e.*, the charge separation developed at the transition state should be negligible. The observed somewhat higher reactivity of 11 than 4 is in accordance with the reactivity sequence reported for a series of alkyl isocyanides,<sup>13</sup> though the rate constant for 11 should be regarded as a very approximate value because of the considerable side reactions. The results in diglyme are of interest because a con-

siderable rate enhancement as well as the formation of a considerable amount of adamantane was observed; these results are quite different from those reported for aromatic isocyanide.<sup>13</sup> The large negative value of  $\Delta S^\ddagger$  suggests a strong solvation at the transition state. Furthermore, 4 rearranges 11 times faster than 11. These facts indicate that the reaction proceeding *via* an ion-pair or a cationic intermediate is involved in a polar solvent such as diglyme. The formation of adamantane might be explained by an initial formation of adamantyl cation followed by hydride abstraction from the solvent or the substrate.

### Experimental Section<sup>21</sup>

**N-1-Adamantylformamide (2).** A powdered mixture of 1-adamantyl bromide (1a, 1.43 g, 20 mmol) and sodium cyanide (6.5 g, 0.13 mol) was added to a stirred sulfuric acid (95%) (100 ml) at room temperature in 2 hr (*Caution!* the reaction should be carried out under a good hood). After stirring was continued for 2 days at room temperature, the mixture was poured onto crushed ice (0.5 kg), neutralized with 20% sodium hydroxide, and extracted with methylene chloride (5 × 80 ml). The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give crude 2, which was recrystallized from *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub> to afford 2 (2.68 g, 75%), mp 140–141° (lit.<sup>4</sup> mp 139–140°).

**B.** A mixture of 1a (3.0 g, 13.1 mmol) in formamide (11.4 g, 253 mmol) was refluxed for 15 hr. The cooled solution was diluted with chloroform (50 ml)-water (50 ml). The organic layer was separated, washed with water (4 × 50 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent and recrystallization of the residue gave 2 (1.54 g, 62%).

**1-Adamantyl Isocyanide (4).** **A.** From 2. A mixture of 2 (0.90 g, 5.9 mmol), triphenylphosphine (1.57 g, 6.0 mmol), carbon tetrachloride (0.77 g, 5.0 mmol), and triethylamine (0.55 g, 5.0 mmol) in chloroform (10 ml) was heated at 60° for 3 hr. After removal of the solvent, the residue was chromatographed on a silica gel column eluting with methylene chloride. The isocyanide 4 was obtained from the first fraction and was recrystallized from light petroleum (bp 40–60°) to give analytically pure 4 (0.59 g, 61%), mp 179–180° (sealed tube).

*Anal.* Calcd for C<sub>11</sub>H<sub>15</sub>N: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.67; H, 9.51; N, 8.90.

**B.** From 1-Adamantanamine (3). A mixture of 3 (150 mg, 1.0 mmol), benzyltriethylammonium chloride (20 mg), and benzene (8 ml) in 50% aqueous potassium hydroxide (9 ml) was stirred vigorously for 30 min at room temperature, and to the resulting emulsion chloroform (179 mg, 1.5 mmol) in benzene (3 ml) was added in 15 min under ice cooling. After stirring was continued for 1 hr under ice cooling and for 4 hr at room temperature, the mixture was diluted with water (10 ml) and the organic layer was separated. The water layer was extracted with benzene (20 ml) and the organic layer was combined with the benzene extracts, washed with water (3 × 10 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent and sublimation of the residue at 80° (30 mm) afforded the isocyanide 4 (87 mg, 54%). The reaction of 3 with dichlorocarbene (3-molar excess) generated from CHCl<sub>3</sub>-*t*-BuOK in *n*-hexane gave 4 in 40% yield.

**1-(1-Adamantyl)tetrazole (5).** To an anhydrous hydrazoic acid solution prepared from sodium azide (1.8 g, 27 mmol), water (1 ml), sulfuric acid (1.32 g, 13.5 mmol), and chloroform (20 ml), dried over Na<sub>2</sub>SO<sub>4</sub><sup>22</sup> was added 4 (0.5 g, 31 mmol). The resulting solution was warmed at 40° for 1 day and the excess hydrazoic acid and the solvent were removed to afford a solid residue (632 mg) which was washed with ether to give pure tetrazole 5 (589 mg, 91%); mp 123–126° (sealed tube); ir (KBr) 3140, 3120, 2920, 2850, 1455, 1345, 1185, and 1105 cm<sup>-1</sup>; uv (EtOH)  $\lambda_{\max}$  274 nm ( $\epsilon$  3) as a shoulder; nmr (CDCl<sub>3</sub>)  $\delta$  8.60 (s, 1 H), 2.40–2.10 (s, 9 H), and 1.90–1.65 (s, 6 H); mass spectrum *m/e* (rel intensity) 204 (M<sup>+</sup>, 53), 179 (57), 149 (51), and 135 (100).

Treatment of 4 with hydrazoic acid in ether in the presence of a catalytic amount of sulfuric acid according to the Zimmerman and Olofson procedure<sup>9</sup> afforded crystalline compounds, mp 134–137 and/or 175–178° dec depending on the reaction conditions, both in 90% yield. These as yet unidentified compounds seem to be dimeric.

**1-(1-Adamantyl)-2,4-dithioxo-1,2,3,4-tetrahydrotriazine (6).** To a stirred mixture of 4 (161 mg, 1.0 mmol), potassium thiocyanate (292 mg, 3.0 mmol), ether (5 ml), and water (3 ml) was added potassium hydrogen sulfate (409 mg, 3.0 mmol) in water (3 ml) under ice-salt bath cooling. After stirring for 30 min, the

mixture was diluted with water (100 ml) and extracted with chloroform (4 × 20 ml). The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to afford yellowish crystals (295 mg), which were recrystallized from MeOH-C<sub>6</sub>H<sub>6</sub> to give 6 as faintly yellowish needles (237 mg, 85%); mp 184–187° dec; ir (KBr) 3200, 1600, and 1105 cm<sup>-1</sup>.

*Anal.* Calcd for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>S<sub>2</sub>: C, 55.90; H, 6.14; N, 15.05. Found: C, 55.97; H, 6.11; N, 15.01.

**N-1-Adamantyl-N'-pentamethyleneformamide (7).** A mixture of 4 (161 mg, 1.0 mmol) and cuprous chloride (15 mg, 0.15 mmol) in piperidine (1.0 ml, 10 mmol) was refluxed for 4 hr. After removal of the excess piperidine by distillation, methylene chloride (5 ml) was added and an insoluble material was removed by filtration. The filtrate was chromatographed on a silica gel column, eluting with chloroform to afford 7 (74 mg, 30%) after recrystallization from *n*-hexane: mp 104–107°; ir (KBr) 1655 cm<sup>-1</sup> (C=N); nmr (CDCl<sub>3</sub>)  $\delta$  3.80 (s, 1 H) and 2.75–1.90 (m, 25 H); mass spectrum *m/e* (rel intensity) 246 (M<sup>+</sup>, 95), 245 (M - 1, 100), 189 (80), 179 (90), 162 (40), 135 (60), and 111 (40).

*Anal.* Calcd for C<sub>16</sub>H<sub>26</sub>N<sub>2</sub>: C, 77.99; H, 10.64; N, 11.37. Found: C, 77.91; H, 10.85; N, 11.24.

In the above reaction, when the reaction mixture stood for 2 days at room temperature, a cuprous chloride complex, mp 235–237°, was obtained as an insoluble portion in methylene chloride. Its structure was not clarified.

**2-Adamantanamine (10).** Adamantanone oxime (2.5 g, 15 mmol) was reduced with lithium aluminum hydride (2.5 g, 66 mmol) in tetrahydrofuran (50 ml) by refluxing for 2 days. The usual work-up and recrystallization from *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub> afforded amine 10 as colorless crystals (1.84 g, 81%); mp 100–103°;<sup>23</sup> ir (KBr) 3320 (NH), 1620, 1550, and 1460 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  3.0 (s, 1 H), 2.6–2.3 (s, 2 H), and 2.2–1.35 (broad s, 14 H).

*Anal.* Calcd for C<sub>10</sub>H<sub>17</sub>N: C, 79.40; H, 11.34; N, 9.26. Found: C, 79.45; H, 11.01; N, 9.54.

**2-Adamantyl Isocyanide (11).** **A.** A mixture of 10 (100 mg, 0.66 mmol), benzyltriethylammonium chloride (10 mg), benzene (5 ml), and 50% aqueous potassium hydroxide (8 ml) was vigorously stirred for 30 min at 30°. To the resulting emulsified mixture was added chloroform (80 mg, 0.67 mmol) in benzene (3 ml) under ice cooling in 1 hr, and the stirring was continued for 2 hr at the same temperature and for a further 2 hr at 30°. The benzene layer was separated, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give crude isocyanide 11, which was purified by sublimation at 80° (30 mm) to afford pure 11 (81 mg, 76%), mp 178–180° (sealed tube).

*Anal.* Calcd for C<sub>11</sub>H<sub>15</sub>N: C, 81.93; H, 9.38; N, 8.69. Found: C, 82.20; H, 9.41; N, 8.70.

**B.** To an ice-cooled and stirred mixture 10 (302 mg, 2.0 mmol) and potassium *tert*-butoxide (1.12 g, 10 mmol) in *n*-hexane (10 ml) was added chloroform (1.0 g, 8.3 mmol) during 1 hr under nitrogen, and stirring was continued for 2 hr at the same temperature and for 1 hr at 25°. The organic layer was separated after dilution of the mixture with water, washed with water, and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent gave crude isocyanide 11 (200 mg), which was purified on a silica gel column, eluting with methylene chloride, followed by sublimation to give pure 11 (113 mg, 35%).

**1-(2-Adamantyl)tetrazole (12).** 11 (161 mg, 1.0 mmol) was treated with a chloroform solution of hydrazoic acid prepared from sodium azide (0.6 g, 9 mmol) as above. The crude product was purified by preparative tlc (silica gel, CHCl<sub>3</sub>) to afford tetrazole 12 (110 mg, 54%) as colorless crystals: mp 130–135°; ir (KBr) 3080, 1475, 1455, and 1100 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  8.70 (s, 1 H), 4.60 (broad s, 1 H), 2.9–2.5 (broad s, 2 H), and 2.4–1.6 (m, 12 H); mass spectrum *m/e* (rel intensity) 204 (M<sup>+</sup>, 10), 190 (14), 179 (8.6), 178 (26), 149 (13), and 135 (100).

**N-2-Adamantylformamide (13).** On standing in the atmosphere at room temperature, 11 was converted almost quantitatively to the formamide 13; mp 164–166°; ir (KBr) 3320, 1660, and 1540 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  7.0–6.6 (broad s, 1 H), 5.95 (s, 1 H), 4.15 (broad d, *J* = 7.5 Hz, 1 H), and 2.2–1.6 (m, 14 H); mass spectrum *m/e* (rel intensity) 179 (M<sup>+</sup>, 98), 135 (100), 94 (99), and 80 (80).

*Anal.* Calcd for C<sub>11</sub>H<sub>17</sub>NO: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.92; H, 9.66; N, 7.54.

**Kinetic Measurement.** Samples of isocyanides (*ca.* 2 mg) were transferred into glass tubes (50 × 6 mm i.d.) and sealed under *ca.* 30 mm. The sealed samples were heated at 200 ± 0.7 or 180 ± 0.7° as described in Table II, removed at intervals of time, and quenched in a water bath. The samples were analyzed after dilution with 0.3 ml of acetone on a 1-m Silicone SE-30 and/or Apie-

zon grease L column. For kinetic runs in diglyme, samples of isocyanides (15 mg) were dissolved in freshly purified diglyme (0.5 ml), heated in a sealed tube, and analyzed at intervals directly by glpc. The peak area factors were calculated according to the chromatographic results of known authentic mixtures of the cyanide and isocyanide. The rate constants were calculated as  $\ln [\text{area (RNC)} + \text{area (RCN)}] / \text{area (RNC)} = kt$ . For the case of the formation of adamantane the area of RCN was corrected by summing the area of adamantane. The results are shown in Table II.

**Registry No.**—1a, 768-90-1; 2, 3405-48-9; 3, 768-94-5; 4, 22110-53-8; 5, 50987-38-7; 6, 50987-39-8; 7, 50987-40-1; 10, 13074-39-0; 11, 50987-41-2; 12, 50987-42-3; 13, 24161-71-5; adamantanone oxime, 4500-12-3.

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## Vilsmeier-Haack Cyclizations. Synthesis of 2-Substituted 3-Dimethylamino-5,6-methylenedioxyindenes and the Corresponding Indanones

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In the presence of the Vilsmeier-Haack reagent, suitably activated styrene analogs afford previously unreported 2-substituted 3-dimethylamino-5,6-methylenedioxyindenes. The indenes were hydrolyzed to the corresponding indanones. This constitutes a new synthesis of indanones. Cinnamaldehydes are also obtained under Vilsmeier-Haack conditions. Reaction conditions and electronic and other structural requirements which govern the formation of cinnamaldehydes and aminoindenes are discussed. Selected cinnamaldehydes were shown to have the *E* configuration by X-ray crystallography. Aminoindenes result from cyclization of Vilsmeier-Haack intermediates (**4**) having the *Z* configuration while aldehydes result from Vilsmeier-Haack intermediates (**4**) having the *E* configuration.

Formylation of  $\pi$ -excessive heteroaromatic and activated benzenoid compounds under Vilsmeier-Haack conditions<sup>2</sup> [ $\text{POCl}_3$ ,  $(\text{CH}_3)_2\text{NCHO}$ ] affords aldehydes.<sup>3-13</sup> Formylation of styrenes affords cinnamaldehydes.<sup>13-15</sup> Definitive studies indicate that the electrophile is **1a**<sup>16</sup> rather than **1b**.<sup>15</sup> Thus, (*E*)-1-(3,4-methylenedioxyphenyl)prop-1-ene<sup>17</sup> (**2**) gives **3** ( $\text{R} = \text{H}$ ;  $\text{R}' = \text{CH}_3$ ), which should lose a proton and provide varying quantities of intermediates (*E*)-**4** ( $\text{R} = \text{H}$ ;  $\text{R}' = \text{CH}_3$ ) and (*Z*)-**4** ( $\text{R} = \text{H}$ ;  $\text{R}' = \text{CH}_3$ ). Hydrolysis of these should yield (*E*)-**5** and (*Z*)-**5**. However, the product appears to be stereochemically homogeneous.<sup>15</sup> Nevertheless, analogs of (*Z*)-**4** suitably activated toward electrophilic aromatic substitution may

be expected to undergo cyclization *via* **6** formed by an-chimerically assisted dissociation of chloride. If sufficiently general, this would represent a facile synthesis for the previously unreported 3-dimethylamino-1-indene system (**7**). This, in turn, would serve as precursor for 2-substituted 1-indanones such as **8**, since treatment of **7** with aqueous hydroxide would isomerize the allylamine double bond and would effect hydrolysis of the resulting enamine.<sup>18</sup>

In this report we describe Vilsmeier-Haack cyclizations leading to aminoindenes (*cf.* **7**) which undergo hydrolysis to indanones (*cf.* **8**) which are desired as intermediates for the synthesis of potential prostaglandin analogs.