

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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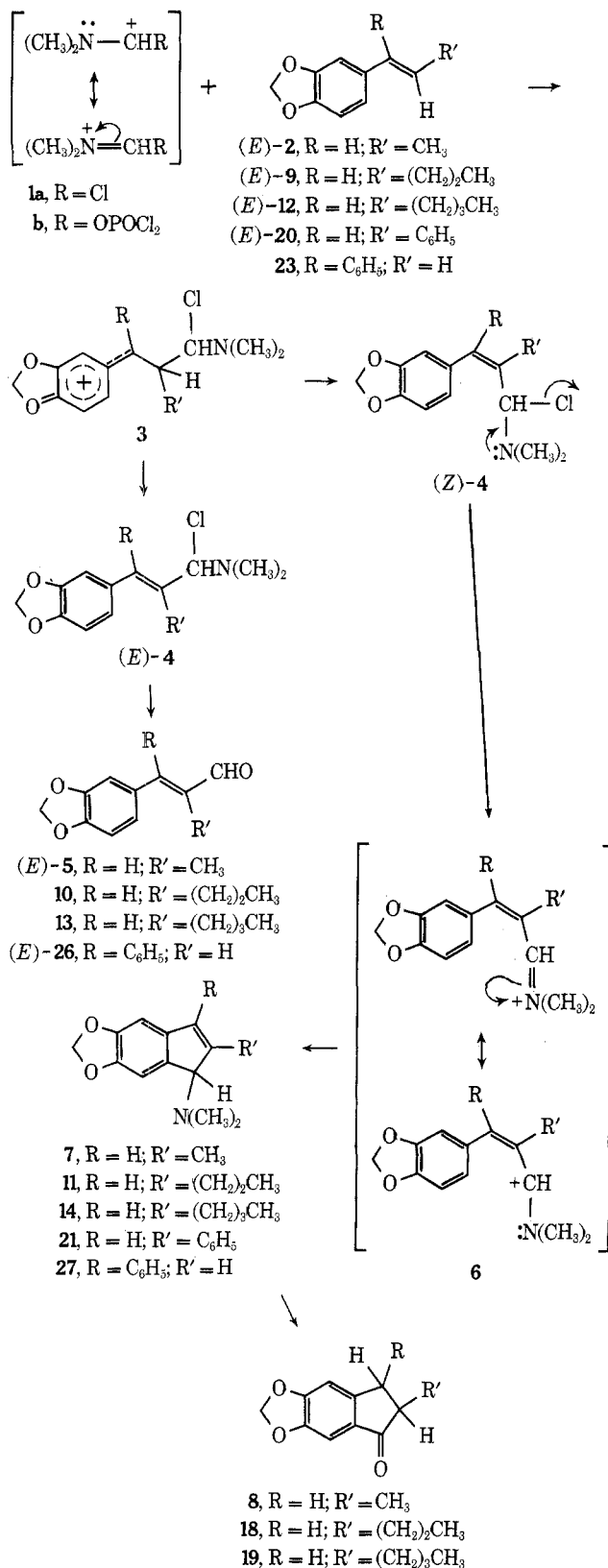
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In the presence of the Vilsmeier-Haack reagent, suitably activated styrene analogs afford previously unreported 2-substituted 3-dimethylamino-5,6-methylenedioxyindenes. The indenes were hydrolyzed to the corresponding indanones. This constitutes a 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 π -excessive heteroaromatic and activated benzenoid compounds under Vilsmeier-Haack conditions² [POCl_3 , $(\text{CH}_3)_2\text{NCHO}$] affords aldehydes.³⁻¹³ Formylation of styrenes affords cinnamaldehydes.¹⁵⁻¹⁵ Definitive studies indicate that the electrophile is **1a**¹⁶ rather than **1b**.¹⁵ Thus, (*E*)-1-(3,4-methylenedioxyphenyl)prop-1-ene¹⁷ (**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.¹⁵ 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.¹⁸

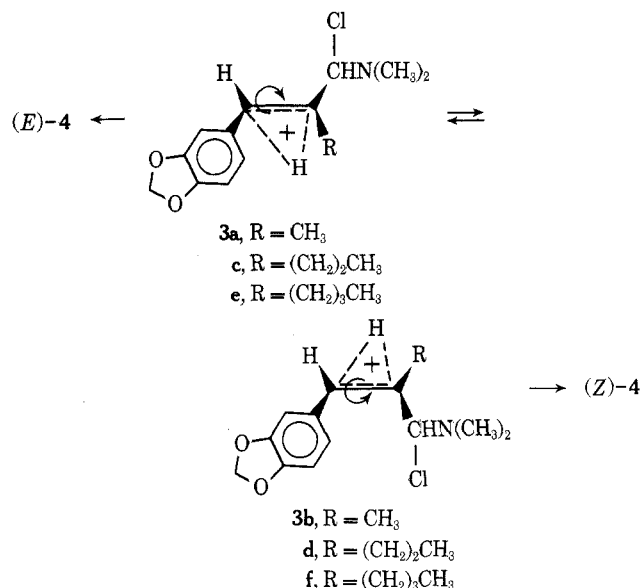
In this report we describe Vilsmeier-Haack cyclizations leading to aminoindenes (*cf.* **7**) which undergo hydrolysis to indanones (*cf.* **8**) which are desired as intermediates for the synthesis of potential prostaglandin analogs.



Results and Discussion

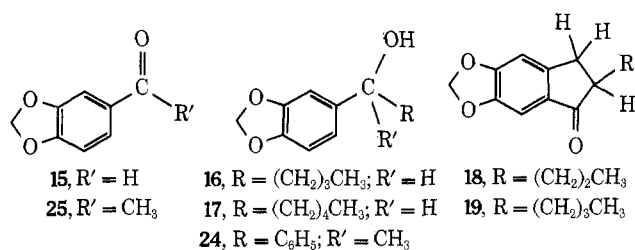
Schmidle and Barnett¹⁵ obtained **5** in 27% yield by adding **2** to the cooled (20°) Vilsmeier-Haack reagent, warming to 55°, maintaining the temperature during the exothermic reaction, and finally heating at 75–80° for 1 hr (method I). The *E* configuration was assigned to **5**.¹⁵ Under these conditions we isolated **5** in 48% yield. No aminoindene (**7**) was detected. The *E* configuration for **5** was substantiated by X-ray crystallography. However, when the reagent-olefin mixture was immediately heated on a

steam bath for 3 hr (method II), **2** afforded 47% of **7** and 23% of (*E*)-**5**. The remainder of the reaction mixture contained starting olefin. The application of first principles of conformational analysis to the formation of (*E*)-**4** and (*Z*)-**4** from **3** (R = H; R' = CH₃) provides an explanation for the change in steric course of the reaction leading to (*E*)-**4** at lower temperatures and to a mixture of (*E*)-**4** and (*Z*)-**4** at higher temperatures. Thus, at lower tempera-



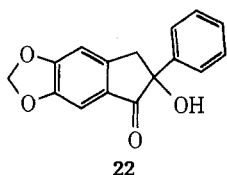
tures, minimization of nonbonded repulsions in **3** requires that product (**4**) develop mainly from **3a** (Ar/Me), the thermodynamically more stable intermediate, to give (*E*)-**4** rather than from **3b** (Ar/ClCHNMe₂) which leads to (*Z*)-**4**.^{19,20} At higher temperatures the relative population of **3b** increases at the expense of **3a** and the product (**4**) contains more (*Z*)-**4** than at lower temperatures. In line with this, method I yields 48% of aldehyde **10** but no indene **11** from olefin (*E*)-**9** while method II affords 71 and 70% of indenes **11** and **14** but, in contrast to treatment of **2** at elevated temperatures, no aldehydes **10** and **13** from olefins (*E*)-**9** and (*E*)-**12**. Thus, the steric bulk of the *n*-propyl and *n*-butyl groups (**3c–f**) reinforces the thermal effects by increasing the relative populations of **3d** and **3f** relative to **3c** and **3e**, lowers the yield of aldehyde precursor [cf. (*E*)-**4**], and increases the yield of indene precursor [cf. (*Z*)-**4**] relative to that obtained from **2**.

Starting olefin [(*E*)-**9**] was prepared in 95% yield by dehydration of **16**, which was obtained in 66% yield by treatment of **15** with *n*-butyllithium. The homolog [(*E*)-**12**] was prepared by dehydration of **17** obtained by treatment of **15** with *n*-pentylmagnesium bromide. Vinyl proton coupling of 15.5 Hz established the *E* stereochemistry of **2**, **9**, and **12**. The aminoindenes (**7**, **11**, **14**) were characterized by conversion to the respective indanones (**8**, **18**, **19**). The nmr spectra (Table I, Experimental Section) are in agreement with the assigned structures. Additional evidence for the structural assignment was obtained from the nmr spectra of the hydrochloride salts of the aminoindenes (**7**,

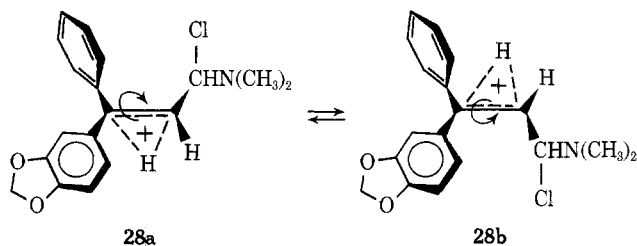


11, 14) (Table II, Experimental Section). Integration of the complex proton resonance multiplets between δ 3.0 and 0.5 ppm accounted for the alkyl and dimethylamino substituents at positions 2 and 3 for each compound. No signals were observed downfield to the aromatic proton resonances H_4 and H_7 . The broad singlets observed at different δ values for H_1 and H_3 define the position of the indene double bond.

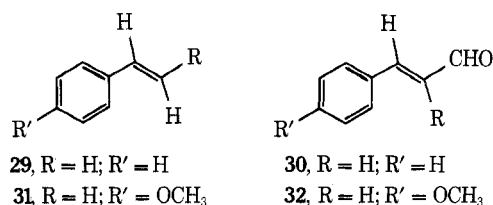
To further investigate the scope of these cyclizations, (*E*)-20^{21,22} was subjected to conditions of method II. The indene 21 was obtained in 16% yield, although the yield could be increased to 25% if (*E*)-20 was added directly to the previously heated (steam bath) Vilsmeier-Haack reagent. Recovery of starting olefin averaged 70%. The indene 21 was characterized by its nmr spectrum (Table II, Experimental Section). The hydrochloride salts of indenones 7, 11, and 14 afforded indanones 8, 18 and 19. 21 as the free base afforded 2-hydroxyindan-1-one 22 which like-



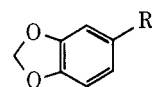
ly results from both hydrolysis and air oxidation in the alkaline medium.²³ This compound was identified by its nmr and mass spectra (Experimental Section). Unlike ketones 8, 18, and 19, 22 did not form a 2,4-dinitrophenylhydrazones.²⁴ Both hydrogen-bonded²⁵ OH stretching (3435 cm^{-1}) and C=O stretching (1685 cm^{-1}) were observed in the infrared spectrum (mull). In contrast to the behavior of 20, 23 prepared by dehydration of 24 obtained by treatment of 25 with phenylmagnesium bromide afforded a 70% yield of aldehyde 26 but no aminoindene 27. The *E* geometry for 26 was established by X-ray crystallography. The crystal conformation of 26 provides an explanation for the steric course of this reaction. Since there is a greater propensity for resonance interaction between the methylenedioxyphenyl ring system and the α,β -unsaturated aldehyde moiety, these groups are more nearly coplanar (25°) than are the phenyl and α,β -unsaturated aldehyde groups (63°). In the intermediate carbonium ion (28) the methylenedioxyphenyl and the contiguous ethyl units should more closely approach coplanarity, while the phenyl and the methylenedioxyphenethyl units should more closely approach 90° . Accordingly, 28a, which leads to aldehyde 26, is more thermodynamically stable than 28b, which leads to indene, since the effective steric bulk of the phenyl moiety in 28a is smaller than that of the methylenedioxyphenyl group of 28b in the direction of the $\text{ClCHN}(\text{CH}_3)_2$ unit.



That activation of the aromatic ring toward electrophilic substitution is a necessary condition for Vilsmeier-Haack cyclizations is indicated by the following. Both methods I and II afford 30 in 42% yield in addition to starting olefin 29 and polymer. No indene could be isolated. Specifically, the effect must be electromeric (*cf.* 6), since 31 affords 32

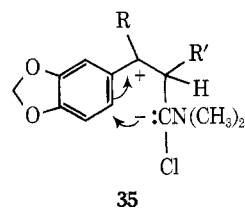


in 68% yield but no indene was isolated.¹⁵ On the other hand, both inductomeric and electromeric effects influence aldehyde formation in the expected manner (*cf.* 3, 28), $\text{OCH}_3 > \text{CH}_3 > \text{H}$.¹⁵ Furthermore, when the exocyclic double bond was isolated from the methylenedioxyphenyl unit, no aldehyde or cyclic products could be detected; 85% of starting olefin 33 and about 5% basic polymer were recovered.



33, R = $\text{CH}_2\text{CH}=\text{CH}_2$
34, R = $\text{CH}_2\text{CH}_2\text{CH}_3$

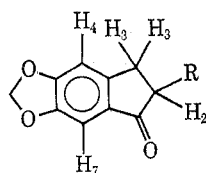
Formylation of the aromatic ring of these styrenes has not been observed. This is not surprising, since the vinyl substituent is expected to deactivate the ring toward electrophilic attack. While this does not argue well for the intermediacy of 6, the cyclization ($4 \rightarrow [6] \rightarrow 7$) may be a concerted process. The fact that 33 and 34 fail to afford aldehydes also suggests an element of steric hindrance (*cf.* ref 12) inherent as well in the styrenes. In addition, initial attack on the ring system fails to explain why the *n*-propyl and *n*-butyl analogs 9 and 12 afford higher yields of indenones (11, 14) than 2 and why 23 affords no indene at all (*cf.* 20 \rightarrow 21). Attack of the vinyl group by carbene²⁶ [$(\text{CH}_3)_2\text{N}\dot{\text{C}}\text{Cl}$] has also been rejected based on the acidity of the medium. In addition, nucleophilic cyclization through the conjugate base of 3 (35) produced in this process lacks precedent.



Finally, recalling that 29 and 31 give 30 and 32 but no indene, this route suggests no decisive role for O(3) and requires a more general scope than can be demonstrated for cyclizations under Vilsmeier-Haack conditions.

In summary, Vilsmeier-Haack cyclization of styrenes to form indenones is facilitated by para-substituents exerting +I or +E effects and requires meta-substituents capable of strong +E effects. Cyclization is promoted by increasing the size of β -alkyl substituents. The mechanism involves electrophilic attack by 1a on the β carbon of the styrene system to give cationic intermediate 3. This undergoes thermally and sterically dependent proton loss (*cf.* 3a-f, 28a,b) to give (*E*)-4, which provides aldehydes of this configuration upon hydrolysis, and (*Z*)-4, which provides the correct juxtaposition of functional groups for cyclization to aminoindenones. Formation of (*Z*)-4 (R = H) is favored at elevated temperatures. Both α - and β -aryl substituents on the starting olefins (*cf.* 20, 23) provide steric as well as electronic constraints which are not completely understood; 20 affords aminoindene 21 but 23 affords only aldehyde 26.

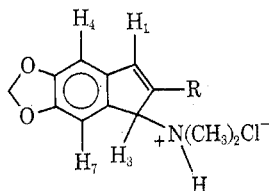
Table I
Conversion of Dimethylaminoindenes to Indanones



2-Substituted 5,6-methylenedioxy- indanone ^b	Yield, %	Mp, °C	Bp, °C (mm)	Chemical shift, ^a δ ppm				
				2H ₃ H ₂	R	OCH ₂ O	H ₄	H ₇
2-Methyl (8) C ₁₁ H ₁₀ O ₃	96-97	63.0-63.5	113-115 (0.025)	2.34-3.55	1.25 (d, $J = 7$ Hz)	6.04	6.79	7.09
2- <i>n</i> -Propyl (18) C ₁₃ H ₁₄ O ₃	96-97	48-49	139.5-140.5 (0.1)	2.35-3.48	0.5-2.0	6.05	6.80	7.06
2- <i>n</i> -Butyl (19) C ₁₄ H ₁₆ O ₃	96-97	46.5-47.5	134-136 (0.03)	2.42-3.50	0.7-2.2	6.05	6.81	7.09

^a Chemical shifts relative to TMS in CDCl₃. ^b Satisfactory elemental analyses were reported for all compounds in the table.

Table II
Conversion of Methylenedioxy Olefins to Aminoindenes



2-Substituted dimethylamino- 5,6-methylenedioxy- ind-1-ene ^f	Yield, %	Mp, °C (HCl salt or free amine)	Bp, °C (mm) of free amine	Chemical shift, δ ppm				
				OCH ₂ O	H ₁	H ₃	H ₄	H ₇
2-Methyl (7) C ₁₃ H ₁₅ NO ₂ Cl	47	188-190 dec (salt)	112-116 (0.15)	5.86 ^a	6.22	3.91	6.63	6.95
2- <i>n</i> -Propyl (11) C ₁₅ H ₂₀ NO ₂ Cl	71	177-178 (salt)	125-127.5 (0.25)	6.01 ^b	6.61	4.82	6.77	7.50
2- <i>n</i> -Butyl (14) C ₁₆ H ₂₂ NO ₂ Cl	70	177-178.5 (salt)	133.5-136 (0.35)	6.00 ^b	6.51	4.80	6.76	7.51
2-Phenyl (21) C ₁₅ H ₁₇ NO ₂	16 ^c 25 ^e	134-135 (amine)	Not distilled	5.90 ^d	6.86	4.62	6.77	7.06

^a Chemical shifts relative to TMS of free base in (CD₃)₂CO. ^b Chemical shifts relative to TMS of HCl salts in CDCl₃. ^c A 16% yield is obtained if the reaction is carried out as described in the Experimental Section. ^d Chemical shifts relative to TMS of free base in CDCl₃. ^e A 25% yield is obtained if olefin 21 is added directly to the previously warmed (steam bath), stirred Vilsmeier-Haack reagent and the mixture subsequently is heated for 3 hr. ^f Satisfactory elemental analyses were reported for all compounds in the table.

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer. Mass spectra were recorded utilizing a Du Pont 21-491 mass spectrometer interfaced with a Hewlett-Packard 2100A computer. All aminoindenes and indanones showed the expected molecular ion. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer. Purity of starting olefins was confirmed using a Hewlett-Packard Model 402 gas chromatograph equipped with a flame ionization detector and glass columns containing 10% Carbowax on Chromosorb W (80-100 mesh). Elemental analyses were performed by Clark Microanalytical Laboratories, Urbana, Ill.

Crystals of 5 and 26 suitable for diffraction study were grown by slow evaporation of hexane solutions at room temperature, mp 64-66 and 96-97°, respectively. Crystal densities of 1.313 and 1.316 g cm⁻³ (23°), respectively, were measured by flotation in KI-H₂O using a Westphal balance. Integrated intensities (I) of reflections of the form hkl and hkl , for which $\sin \theta \leq 0.91$, were collected in the θ - 2θ mode with a Nonius CAD-IV automated diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å). Integrated intensities less than $2\sigma(I)$ were considered unobservably weak and were arbitrarily assigned values of $\sigma(I)/2$. The atomic scattering factors were taken from the International Tables for X-ray crystallography.²⁷ Computer programs used in this study were written for the IBM 1130 and PDP 10 systems.²⁸ Both structures were

solved with the aid of MULTAN.^{28,29} The block-diagonal, least-squares procedure was used to refine atomic positional and thermal parameters. Hydrogen atoms were refined isotropically ($b = 5.0$ Å²).

The final tables of structure factors, atomic positional and thermal parameters, bond lengths and angles, and other conformational detail will appear in the definitive report of the crystal structures of 5 and 26.³⁰

A. Source or Synthesis of Starting Olefins. (*E*)-1-(3,4-Methylenedioxyphenyl)prop-1-ene (isosafrrole, 2) was purchased from Pfaltz and Bauer, Flushing, N. Y., and was used without further purification.

(*E*)-1-(3,4-Methylenedioxyphenyl)pent-1-ene (9). *n*-Butyllithium (0.43 mol) in hexane (120 ml, 21.4% *n*-BuLi) was added by syringe in 30-ml portions to a stirred solution of 30 g (0.20 mol) of piperonal (15) (Pfaltz and Bauer) in 300 ml of anhydrous Et₂O maintained at -78° under a N₂ atmosphere. The mixture was allowed to warm to room temperature while stirring overnight. The mixture was cooled to -10° and saturated NaCl solution (100 ml) was added to decompose the excess *n*-BuLi. The aqueous layer was extracted with Et₂O (175 ml) and the organic layer was washed with H₂O and saturated NaCl solution, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The resulting viscous brown oil was distilled, affording 27.6 g (66.3%) of a yellow oil [1-(3,4-methylenedioxyphenyl)pentan-1-ol] (16), bp 112-114° (0.1 mm). Redistillation through a 12-in. Vigreux col-

umn afforded alcohol, bp 113.5–115.5° (0.15 mm), which was 95% pure (glpc). A solution of this alcohol (12.0 g, 0.06 mol) and *p*-toluenesulfonic acid (0.75 g, 0.004 mol) in benzene (300 ml) was allowed to reflux until no H₂O was collected in a Dean-Stark trap (ca. 30 min). The reaction mixture was diluted with 250 ml of Et₂O, washed with H₂O, dried over anhydrous MgSO₄, and concentrated under reduced pressure. Distillation of the yellow residue afforded 10.4 g (95.0%) of a colorless liquid (9): bp 90–92° (0.3 mm); nmr (CDCl₃) δ for the calculated ABX₂ spectrum shows eight lines for the AB part (AB, 2 H, vinyl protons), δ_A 6.24, δ_B 5.98, and (X, 2 H, CH₂CH₂CH₃) δ_X 2.12 with $J_{AB} = 15.5$, $J_{AX} = 0$, $J_{BX} = 5.5$ –6.0 Hz; δ 0.95 (t, 3 H, CH₃, $J_{CH_2Me} = 6.5$ Hz), 1.47 (sextet, 2 H, CH₂CH₂CH₃, $J_{CH_2CH_2} = 5.5$ –6 Hz), 6.6–6.9 (m, 3 H aromatic).

Anal. Calcd for C₁₂H₁₄O₂: C, 75.8; H, 7.42. Found: C, 75.70; H, 7.45.

(*E*)-1-(3,4-Methylenedioxyphenyl)hex-1-ene (12). To a stirred mixture (maintained in a dry atmosphere) containing 100 ml of anhydrous Et₂O and 9.3 g (0.4 g-atom) of Mg (turnings) was added dropwise 60.4 g (0.4 mol) of 1-bromopentane. After the addition, the stirred mixture was refluxed for an additional 30 min to dissolve all remaining metal. The brown solution was cooled to 0° and piperonal (15, 60.0 g, 0.4 mol) dissolved in 200 ml of anhydrous Et₂O was added dropwise with stirring. After 1 hr the mixture was extracted with two 150-ml portions of saturated NH₄Cl solution. The aqueous layers were washed with 150 ml of Et₂O and the combined Et₂O solutions were washed with saturated NaCl solution, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was distilled, affording 60.9 g (68.4%) of a viscous oil (17).

1-(3,4-methylenedioxyphenyl)hexan-1-ol (17) had bp 135–138° (0.35 mm). Redistillation through a 12-in. Vigreux column afforded alcohol 17, bp 113–115° (0.12 mm), which was 96% pure (glpc). Dehydration of this alcohol under conditions described for the preparation of 9 afforded 12, bp 108–110° (0.3 mm), in 92% yield. The sample was 96% pure (glpc). Redistillation (spinning-band column) afforded 12, bp 95–97° (0.15 mm), in analytically pure form: nmr (DCCl₃) δ for the calculated ABX₂ spectrum shows eight lines for AB part (AB, 2 H, vinyl protons), δ_A 6.21, δ_B 6.04, and (X, 2 H, CH₂CH₃) δ_X 2.14 with $J_{AB} = 15.5$, $J_{AX} = 0$, $J_{BX} = 5.5$ Hz; δ 0.7–1.65 (m, 9 H, CH₂CH₂CH₂CH₃), 6.6–6.9 (m, 3 H, aromatic).

Anal. Calcd for C₁₃H₁₆O₂: C, 76.4; H, 7.90. Found: C, 76.15; H, 8.08.

(*E*)-1-(3,4-Methylenedioxyphenyl)-2-(phenyl)ethene (20) was prepared according to the method of Tiffeneau and Levy^{21,22} affording pale yellow needles (50%), mp 91–92° (lit.²¹ mp 94–95°, lit.²² mp 93–94°).

Anal. Calcd for C₁₅H₁₂O₂: C, 80.3; H, 5.39. Found: C, 79.94; H, 5.72.

1-(3,4-Methylenedioxyphenyl)-1-(phenyl)ethene (23). To 3,4-methylenedioxyacetophenone³¹ (25, 7.5 g, 0.046 mol), mp 84.5–85.5° (lit.³¹ mp 85°, lit.³² mp 83–84°), in benzene (100 ml) was added phenylmagnesium bromide (0.06 mol in 100 ml of Et₂O). After the usual work-up the resulting tertiary alcohol 24 was dehydrated under conditions described for the preparation of 9. Distillation afforded 8.2 g (78.5%) of 23: bp 124–126° (0.25 mm); nmr (CDCl₃) δ 5.32 (broad s, 2 H, vinyl H's), 5.74 (s, 2 H, OCH₂O), 6.5–6.9 (m, 3 H, Ar), 7.26 (broad s, 5 H, Ph).

Anal. Calcd for C₁₅H₁₂O₂: C, 80.3; H, 5.39. Found: C, 80.38; H, 5.28.

B. General Procedure for Vilsmeier-Haack Cyclization (Method II). To a cooled (ice bath), round-bottom flask containing dimethylformamide (DMF) (45 g, 0.61 mol) was added dropwise with stirring POCl₃ (18.4 g, 0.12 mol). The mixture was stirred in an ice bath for 15–20 min and the olefin (0.10 mol) was added dropwise. After the addition, the reaction mixture was immediately heated on a steam bath for 3 hr. The resulting black mixture was poured into 400 ml of ice-H₂O and unreacted olefin was removed by extraction with two 175-ml portions of Et₂O. The aqueous layer was made basic by the addition of 10% aqueous NaOH solution and any aminoindenes were extracted with three 150-ml portions of Et₂O. The combined Et₂O layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure. Distillation of volatile aminoindenes 7, 11, and 14 afforded yellow liquids which were air sensitive and decomposed upon standing at room temperature. The amines were converted to the stable HCl salts, which were recrystallized as white solids from EtOH-Et₂O. The free amine, 2-phenyl-3-dimethylamino-5,6-methylenedioxyind-1-ene (21), was not distilled. It was stable and could be crystallized from low-boiling petroleum ether containing a small

amount of benzene (decolorized with charcoal). Physical constants and analytical data for the aminoindenes 7, 11, 14, and 21 and the hydrochloride salts are listed in Table II.

C. Aldehyde Products Obtained during Vilsmeier-Haack Reactions. (*E*)-2-Methyl-3-(3,4-methylenedioxyphenyl)acrylaldehyde (5) was isolated in 48% yield when 2 served as starting olefin and the reaction was carried out according to Schmidle and Barnett¹⁵ (method I). Recrystallization from benzene-hexane afforded crystals, mp 64–66.5° [lit.¹⁵ bp 110–130° (0.1 mm)]. When the reaction was carried out under Vilsmeier-Haack cyclization conditions (method II, above) 5 was isolated in 23% yield by distillation of the residue resulting from ether extraction of the H₂O-diluted reaction mixture.

2-*n*-Propyl-3-(3,4-methylenedioxyphenyl)acrylaldehyde (10) was prepared from 3.85 g (0.03 mol) of POCl₃, 7.3 g (0.1 mol) of DMF, and 4.75 g (0.03 mol) of 9 according to the method of Schmidle and Barnett¹⁵ (method I), affording 2.6 g (48%) of yellow oil, bp 115–117° (0.1 mm).

Anal. Calcd for C₁₃H₁₄O₃: C, 71.55; H, 6.42. Found: C, 71.24; H, 6.35.

(*E*)-3-Phenyl-3-(3,4-methylenedioxyphenyl)acrylaldehyde (26). Treatment of olefin 23 (2.2 g, 0.01 mol), DMF (4.5 g, 0.061 mol), and POCl₃ (1.84 g, 0.012 mol) as described under method II affords, after addition of NaOH to the aqueous layer and extraction with ether, 1.75 g (69.5%) of 26 as pale yellow needles (hexane-benzene): mp 97–98° (2,4-DNPH mp 233–235° dec); nmr (CDCl₃) δ 5.97 (s, 2 H, OCH₂O), 6.34 (d, 1 H, vinyl, $J_{H-CHO} = 8$ Hz), 9.43 (d, 1 H, CHO), 6.7–6.9 (m, 3 H, Ar), 7.1–7.6 (m, 5 H, Ph). No aminoindene was detected and 0.22 g of polymer formed during the reaction.

Anal. Calcd for C₁₆H₁₂O₃: C, 76.2; H, 4.79. Found: C, 76.34; H, 4.87.

Cinnamaldehyde (30). In methods I and II, styrene (29, 10.4 g, 0.10 mol), DMF (50 g, 0.68 mol), and POCl₃ (20 g, 0.13 mol) afforded 5.5 g (41.6%) of 30, bp 84–87° (2.0 mm) [lit.¹⁵ bp 84–87° (2.0 mm)]. Glpc analysis showed the remaining portion of the reaction mixtures to be styrene (29).

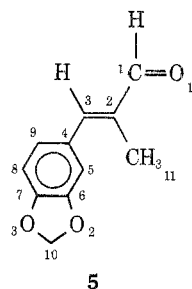
D. Conversion of 2-Substituted 3-Dimethylamino-5,6-methylenedioxyind-1-enes 7, 11, and 14 to 2-Substituted 5,6-Methylenedioxy-1-indanones 8, 18, and 19, Respectively. The HCl salts of aminoindenes 7, 11, and 14 (0.02 mol) were dissolved in a solution of NaOH (10.0 g, 0.25 mol) in 200 ml of H₂O-EtOH (1:1), stirred at room temperature overnight, diluted with 200 ml of H₂O, and extracted with three 75-ml portions of Et₂O. The combined Et₂O layers were washed with saturated NaCl solution (100 ml), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The yellow residue was distilled under reduced pressure, affording nearly colorless liquids which crystallized on cooling. The distillates were recrystallized from petroleum ether (bp 30–60°) or petroleum ether-benzene, affording white, crystalline samples of indanones 8, 18, and 19, respectively. Physical constants and analytical data for the indanones are listed in Table I.

E. Conversion of 2-Phenyl-3-dimethylamino-5,6-methylenedioxyind-1-ene (21) to 2-Phenyl-2-hydroxy-5,6-methylenedioxy-1-indanone (22). A solution of NaOH (4.0 g, 0.1 mol) in 80 ml of H₂O-EtOH (1:1) was added to 21 (1.14 g, 0.004 mol). The mixture was stirred at room temperature overnight, diluted with H₂O, and extracted with three 100-ml portions of Et₂O. The combined Et₂O layers were washed with 100 ml of saturated NaCl solution, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The brown solid residue (0.6 g, 0.002 mol, 50%) was recrystallized from absolute EtOH, affording pale yellow needles (22): mp 169.5–170.5°; nmr (DMSO-*d*₆) δ 7.29 (s, 5 H, aromatic), 7.12 (s, 1 H, H₇ proton), 7.08 (s, 1 H, H₄ proton), 6.19 (s, 2 H, OCH₂O), 6.22 (s, 1 H, -OH exchangeable with D₂O), 3.46 and 3.42 (d, 2 H, geminal H₃ protons); mass spectrum (70 eV) *m/e* (rel intensity) 268 (35), 135 (11), 105 (base), 77 (30).

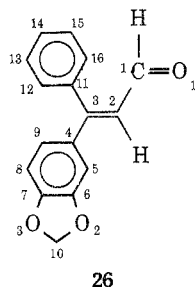
Anal. Calcd for C₁₆H₁₂O₄: C, 71.6; H, 4.47. Found: C, 71.58; H, 4.59.

F. X-Ray Diffraction Study of 5. The material crystallizes in monoclinic space group *P*₂₁/*n*. The unit cell parameters are: *a* = 5.082 (2), *b* = 8.578 (3), *c* = 22.016 (7) Å, $\beta = 96.38$ (1)°. The theoretical density is 1.324 g cm⁻³, corresponding to four molecules per unit cell. Other than systematic absences there are 592 out of 1621 measured independent reflections for which $(I) < 2\sigma(I)$. The structure was solved using 201 of the highest (>1.60) renormalized $|E|$ values. An *E* map afforded positions for all nonhydrogen atoms. Refinement of atomic positional and thermal parameters converged at $R_{\text{all}}^{33} = 0.128$ and $R_{\text{obsd}} = 0.095$. Hydrogen atoms were located in a difference Fourier map. The final cycles of re-

finement converged at $R_{\text{all}} = 0.075$ and $R_{\text{obsd}} = 0.039$. The calculated C(1)-C(2)-C(3)-C(4) torsion angle of $+177.3$ (3) $^\circ$ clearly establishes the *E* geometry shown in **5**. The angle between the normals to the least-squares planes defined by the methylenedioxyphenyl and the O(1)-C(1)-C(2)-C(3)-C(4) systems is 5.1° .



G. X-Ray Diffraction Study of 26. The material crystallizes in monoclinic space group $P2_1/n$. The unit cell parameters are: $a = 6.310$ (3), $b = 8.939$ (4), $c = 22.572$ (8) \AA , $\beta = 97.75$ (1) $^\circ$. The theoretical density is 1.328, corresponding to four molecules per unit cell. Other than systematic absences there are 462 out of 2185 measured independent reflections for which $(I) < 2\sigma(I)$. The structure was solved using 220 of the highest (>1.70) renormalized $|E|$ values. An *E* map afforded positions for all nonhydrogen atoms. Refinement of atomic positional and thermal parameters converged at $R_{\text{all}} = 0.119$ and $R_{\text{obsd}} = 0.106$. Hydrogen atoms were located in a difference Fourier map. The final cycles of refinement converged at $R_{\text{all}} = 0.052$, $R_{\text{obsd}} = 0.039$. The calculated C(1)-C(2)-C(3)-C(4) torsion angle of -173.4 (2) $^\circ$ clearly establishes the *E* geometry in **26**. The angles between the normals (*N*) to the least-squares planes defined by the methylenedioxyphenyl (N_1), O(1)-C(1)-C(2)-C(3)-C(4)-C(11) (N_2) and phenyl (N_3) systems are: $N_1-N_2 = 24.7^\circ$, $N_2-N_3 = 62.7^\circ$, and $N_1-N_3 = 74.8^\circ$.



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Registry No.—(*E*)-**5**, 51003-21-5; **7**, 51003-77-1; **7** hydrochloride, 51003-78-2; **8**, 51003-79-3; (*E*)-**9**, 51003-18-0; (*E*)-**10**, 51021-63-7; **11**, 51003-80-6; **11** hydrochloride, 51003-81-7; (*E*)-**12**, 51003-17-9; **14**, 51003-82-8; **14** hydrochloride, 51003-83-9; **15**, 120-57-0; **16**, 5422-01-5; **17**, 6412-93-7; **18**, 51003-84-0; **19**, 51003-85-1; (*E*)-**20**, 51003-16-8; **21**, 51003-86-2; **22**, 51003-87-3; **23**, 51003-88-4; **25**, 3162-29-6; (*E*)-**26**, 51003-15-7.

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