four times). *Anal.* Calcd for $C_{20}H_{13}ClN_2O \cdot HCl$: C, 64.9; H, 4.1; Cl, 19.2; N, 7.6. Found: C, 64.7; H, 4.0; Cl, 19.0; N, 7.8.

Treatment of 0.090 g of **5c** HCl in ethanol with 2 *N* NaOH gave 0.055 g (68%) of **5c**: mp 222–223° (from ethanol–water); ir (Nujol) 3060 (OH), 1660 cm^{-1} (C=N or C=O); uv λ_{max} 248 nm (ϵ 18,700) 261 (19,690), 305 infl (12,160). *Anal.* Calcd for $C_{20}H_{13}ClN_2O$: C, 72.2; H, 3.9; Cl, 10.7; N, 8.4. Found: C, 71.9; H, 4.1; Cl, 11.0; N, 8.4.

B. From Oxidation of 5e.—A solution of 0.30 g (0.0095 mol) of **5e** in 10 ml of anhydrous DMF was added to 0.06 g (0.0025 mol) of sodium hydride and stirred at room temperature. The resultant red solution was treated with a stream of dry air until the color had disappeared. The solution was poured on ice water to give 0.21 g (67%) of **5c**: mp 222–224° (ethanol–water); nmr, uv, and ir identical with spectra obtained from **5c** from **5a**; mmp 224–225°.

11-Phenyl-11*H*-isoindolo[2,1-*a*]benzimidazol-11-ol (5d).—A solution of 0.5 g of **5b** in 10 ml of 2 *N* hydrochloric acid was allowed to stand at room temperature for 1.5 hr. The resultant solid was filtered off to give 0.4 g (71%) of **5d** HCl, mp 288–290°. *Anal.* Calcd for $C_{20}H_{14}N_2O \cdot HCl$: C, 71.7; H, 4.5; Cl, 10.6. Found: C, 72.1; H, 4.7; Cl, 10.3.

Treatment of a solution of 0.1 g of **5d** HCl in ethanol with 2 *N* NaOH gave 0.070 g (79%) of **5d**: mp 223–225° (ethanol–water) (lit.[3] mp 220–221°); ir (Nujol) 3060 (OH), 1655 cm^{-1} (C=N); uv λ_{max} 242 nm (ϵ 19,240), 291 (12,300), 305 infl (11,420). *Anal.* Calcd for $C_{20}H_{14}N_2O$: C, 80.5; H, 4.7; N, 9.4. Found: C, 80.9; H, 4.8; N, 9.7.

11-(*p*-Chlorophenyl)-11*H*-isoindolo[2,1-*a*]benzimidazole (5e).—To a stirred suspension of 2.16 g (0.02 mol) of *o*-phenylenediamine in 50 ml of water, sufficient concentrated hydrochloric acid was added to obtain a clear solution. To this a solution of 4.89 g (0.02 mol) of 2-(*p*-chlorobenzoyl)benzaldehyde[12] (mp 108–110°) in 100 ml of acetic acid was added. The resulting solution was held at 80° for 15 min and then concentrated under reduced pressure. The residue was treated first with ethanol followed by ether to give 4.3 g (61%) of **5e** HCl, mp 268–271° (ethanol–ether). Treatment of 1.0 g of **5e** HCl with 2 *N* NaOH gave 0.80 g (89%) of **5e**: mp 207–208° (from ethanol–water); nmr ($CDCl_3$) δ 6.07 (1, s, C_{11} H), 6.8–8.2 (12, m, aromatic); ir (CH_2Cl_2) 1622 cm^{-1} (C=N); uv λ_{max} 222 nm (ϵ 33,420), 242 (14,820), 251 (9660), 306 (22,300), 319 (18,170). *Anal.* Calcd for $C_{20}H_{13}ClN_2$: C, 75.8; H, 4.1; N, 8.8. Found: C, 75.8; H, 4.3; N, 8.8.

1-(*p*-Chlorophenyl)-3-(β-diethoxyethylamino)-1-methoxy-1*H*-isoindole (6).—A mixture of 7.1 g (0.023 mol) of **4a** and 11 g (0.053 mol) of aminoacetaldehyde diethyl acetal was refluxed in 250 ml of absolute ethanol for 4 hr under an atmosphere of nitrogen. The solvent was evaporated under reduced pressure to yield 5.5 g (60%) of **6**: mp 113–114° (ether–pentane); nmr ($CDCl_3$) δ 1.18 (3, t, J = 7 Hz, CH_2CH_3), 1.23 (3, t, J = 7 Hz, CH_2CH_3), 3.10 (3, s, OCH_3), 3.40–4.0 (6, m, 2 CH_2CH_3, NCH_2), 4.79 (1, t, J = 5 Hz, –CHO), 5.4 (1, broad, NH), 7.1–7.6 (8, m, aromatic); ir (CH_2Cl_2) 3440 (NH), 1672 (weak), 1640 cm^{-1}; uv λ_{max} 227 nm (ϵ 24,200). *Anal.* Calcd for $C_{21}H_{23}ClN_2O_3$: C, 64.9; H, 6.5; N, 7.2. Found: C, 65.2; H, 6.8; N, 7.2.

Acknowledgment.—We would like to thank Dr. S. Barcza and his staff for recording the spectra.

Registry No.—**3a**, 730-77-8; **3b**, 28489-08-9; **4a**, 41581-41-3; **4b**, 41581-42-4; **5a**, 41581-43-5; **5b**, 41581-44-6; **5c**, 41581-45-7; **5c** HCl, 41581-46-8; **5d**, 41581-47-9; **5d** HCl, 41581-48-0; **5e**, 41581-49-1; **5e** HCl, 41581-50-4; **6**, 41581-51-5; **7a**, 14539-29-8; **7a** HCl, 41581-53-7; 3-*p*-chlorophenyl-3-hydroxyphthalimidine, 956-92-3; 3-phenyl-3-hydroxyphthalimidine, 6637-53-2; 2-(*p*-chlorobenzoyl)benzaldehyde, 23864-94-0.

(12) Prepared in analogy to the known 2-benzoylbenzaldehyde; *cf.* ref 2.

The Synthesis of the 3a,8a-Dihydrofuro[2,3-*b*]benzofuran-2(3*H*)-one and 1,3,3a,8a-Tetrahydro-2*H*-benzofuro[2,3-*b*]pyrrol-2-one Ring Systems from 4-Formylcoumarin *via* Acyllactone and Iminelactone Rearrangements

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Syntheses of 3a,8a-dihydrofuro[2,3-*b*]benzofuran-2(3*H*)-ones and 1,3,3a,8a-tetrahydro-2*H*-benzofuro[2,3-*b*]-pyrrol-2-ones by acyllactone and iminelactone rearrangements, respectively, are described.

The rearrangement of α-acyllactones is a well-known synthetic method which has received considerable attention over the past few years for the synthesis of various heterocyclic systems.[1,2] In contrast, there are only two examples of the rearrangement of β-acyl-δ-lactones. Lawson[3] rearranged 4-acetyl-3,4-dihydrocoumarin to 2-methylbenzofuran-3-acetic acid with 3 *N* hydrochloric acid, and Buchi[4] rearranged 4-formyl-5-benzyloxy-7-methoxycoumarin to 4-benzyloxy-6-methoxy-2-oxo-2,3,3a,8a-tetrahydrofuro[2,3-*b*]benzofuran. The difficulties in synthesizing β-acyl-δ-lactones are the probable[3,5] reason for this disparity.

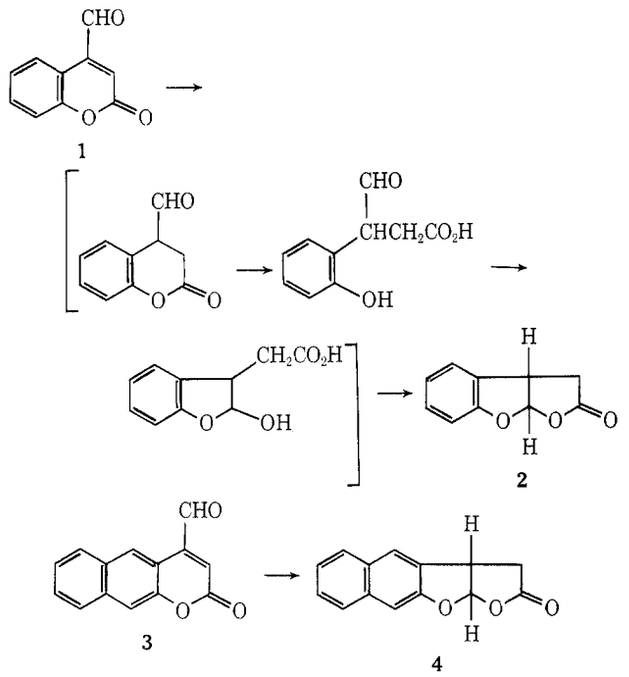
Our earlier work[6] resulted in the first general synthesis of 4-formylcoumarins and made them readily available starting materials to investigate the scope of the rearrangement. The 4-formylcoumarins (**1** and **3** Scheme I) were reduced and rearranged with zinc in acetic acid at 100° to give the expected products (**2** and **4**, respectively). The products are readily converted to benzofuran-3-acetic acids[7] and could also serve as potential intermediates for the synthesis of certain indole alkaloids. Benzofuran derivatives were not detected as by-products from the rearrangement, indicating the ease of formation of the five-membered lactone ring under the reaction conditions.

We were particularly interested in extending the rearrangement to molecules in which the C=O bond of the aldehyde is replaced by C=N. Thus, we subjected imines **5a** and **5b**, oximes **7** and **14**, phenylhydrazone (**16**), and 4-formylcoumarin semicarbazone to the rearrangement conditions.

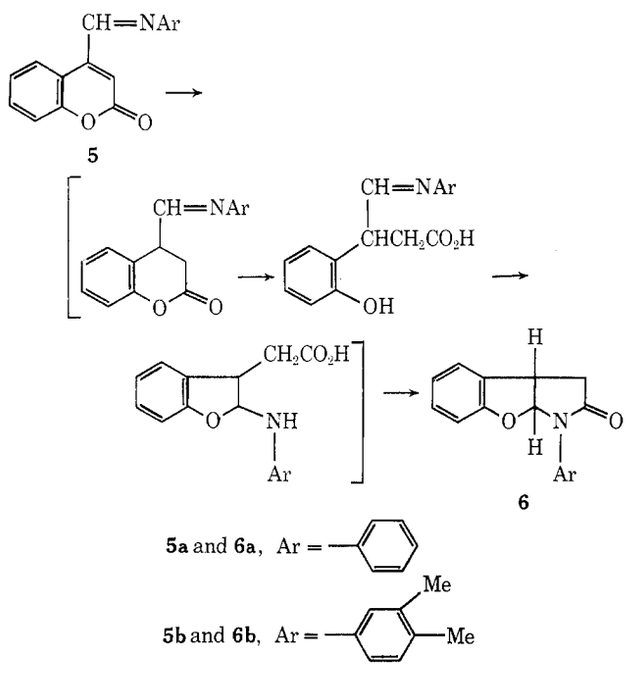
The imines **5a** and **5b** (Scheme II) were reduced and rearranged to give the pyrrolones **6a** and **6b**, respectively. To our knowledge this constitutes the first case

(1) F. Korte and K. H. Buchel in "Newer Methods of Preparative Organic Chemistry," Vol. III, Academic Press, New York, N. Y., 1964, p 199.
(2) H. Wamhoff and F. Korte, *Synthesis*, **4**, 151 (1972).
(3) A. Lawson, *J. Chem. Soc.*, 144 (1957).
(4) G. Buchi, D. M. Foulkes, M. Kurono, G. F. Mitchell, and R. S. Schneider, *J. Amer. Chem. Soc.*, **89**, 6745 (1967).
(5) A. Schiavello and E. Cingolani, *Gazz. Chim. Ital.*, **81**, 717 (1951).
(6) M. von Strandtmann, D. T. Connor, and J. Shavel, Jr., *J. Heterocycl. Chem.*, **9**, 175 (1972).
(7) D. T. Connor and M. von Strandtmann, unpublished work.

SCHEME I



SCHEME II



of an imine–lactone rearrangement and the first synthesis of this ring system. The pyrrolones **6a** and **6b** could also be obtained by the reaction of **2** with corresponding amines, but the overall yields were lower by this route.

The oxime **7** was treated with zinc and acetic acid in the expectation of obtaining hydroxamic acid derivative **8**. The only product isolated was condensation product **13** (Scheme III). Similarly, oxime **14** yielded only condensation product **15**.

Scheme III depicts the probable mechanism for the formation of **13** from **7**. It appears that there is an equal probability for the reduction of either the 3,4 double bond or the C=N double bond resulting in the production of approximately equal amounts of **9** and **10**, which condense to give **11**. The normal cyclization occurs to give **12**, which cyclizes with the net loss of hydroxylamine to give **13**. **8** (or a molecule derived from **8**) would be the major product if the 3,4 double bond were reduced more rapidly than the C=N double bond. **10** would be the major product if the reverse was true.[8] The analytical and spectral data are in agreement with the proposed structure **13**.

The rearrangement of the phenylhydrazone **16** gave a mixture of acetanilide (65%), **20** (6%), and **6a** (25%). The reaction was more complex than in the previous examples. Thin layer chromatography indicated two other compounds present which were not isolated in pure form. It is clear from the products isolated that, as in the case of the oxime **7** rearrangement, the 3,4 double bond and the C=N double bond are competitively reduced. The probable pathway is outlined in Scheme IV.

Reduction of the C=N double bond yields a mixture of aniline and amine **10**, which is acetylated to give the observed products acetanilide and **20**, respectively. Reduction of the 3,4 double bond yields **17**, which condenses with aniline to give **18**. The normal cyclization to give **19**, followed by cyclization with the net loss of phenylhydrazine, yields the observed product **6a**.

4-Formylcoumarin semicarbazone gave an intractable mixture when subjected to the rearrangement conditions.

Experimental Section

Melting points were measured with a Thomas-Hoover capillary melting point apparatus without correction. Nmr spectra were recorded on a Varian A-60 spectrometer with TMS used as internal standard. Infrared spectra were recorded on a Baird Model 455 spectrophotometer. Ultraviolet spectra were recorded on a Beckman DK-I spectrophotometer. Mass spectra were obtained with an AE1 MS-902 instrument.

General Procedure for the Preparation of Imines.—A mixture of 4-formylcoumarin (0.01 mol) and the corresponding amine (0.01 mol) in benzene (50 ml) was refluxed under a water separator for 3 hr. The solvent was removed under reduced pressure to give a solid product.

4-[(Phenylimino)methyl]coumarin (5a).—Yellow crystals recrystallized from ethyl acetate to give **5a** (80%): mp 148–150°; λ_{max}^{EtOH} 240 mμ (ε 15,000), 302 (11,500); ν_{max}^{Nujol} 1720 cm^{-1} (lactone C=O); nmr ($CDCl_3$) δ 8.66 (d, 1, J = 10 Hz, C_5 H), 8.50 (s, 1, HC=N), 7.60–7.10 (m, 8, ArH), and 6.75 (s, 1, C_3 H).

Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.80; H, 4.53; N, 5.42.

4-{[(3,4-Dimethylphenyl)imino]methyl}coumarin (5b).—Yellow crystals recrystallized from ethyl acetate to give **5b** (85%): mp 146–148°; λ_{max}^{EtOH} 245 mμ (ε 12,400), 315 (12,000); ν_{max}^{Nujol} 1720 cm^{-1} (lactone C=O); nmr ($CDCl_3$) δ 8.70 (d, 1, J = 9 Hz, C_5 H), 8.50 (s, 1, HC=N), 7.75–7.10 (m, 6, ArH), 6.82 (s, 1, C_3 H), and 2.36 (s, 6, CH_3–).

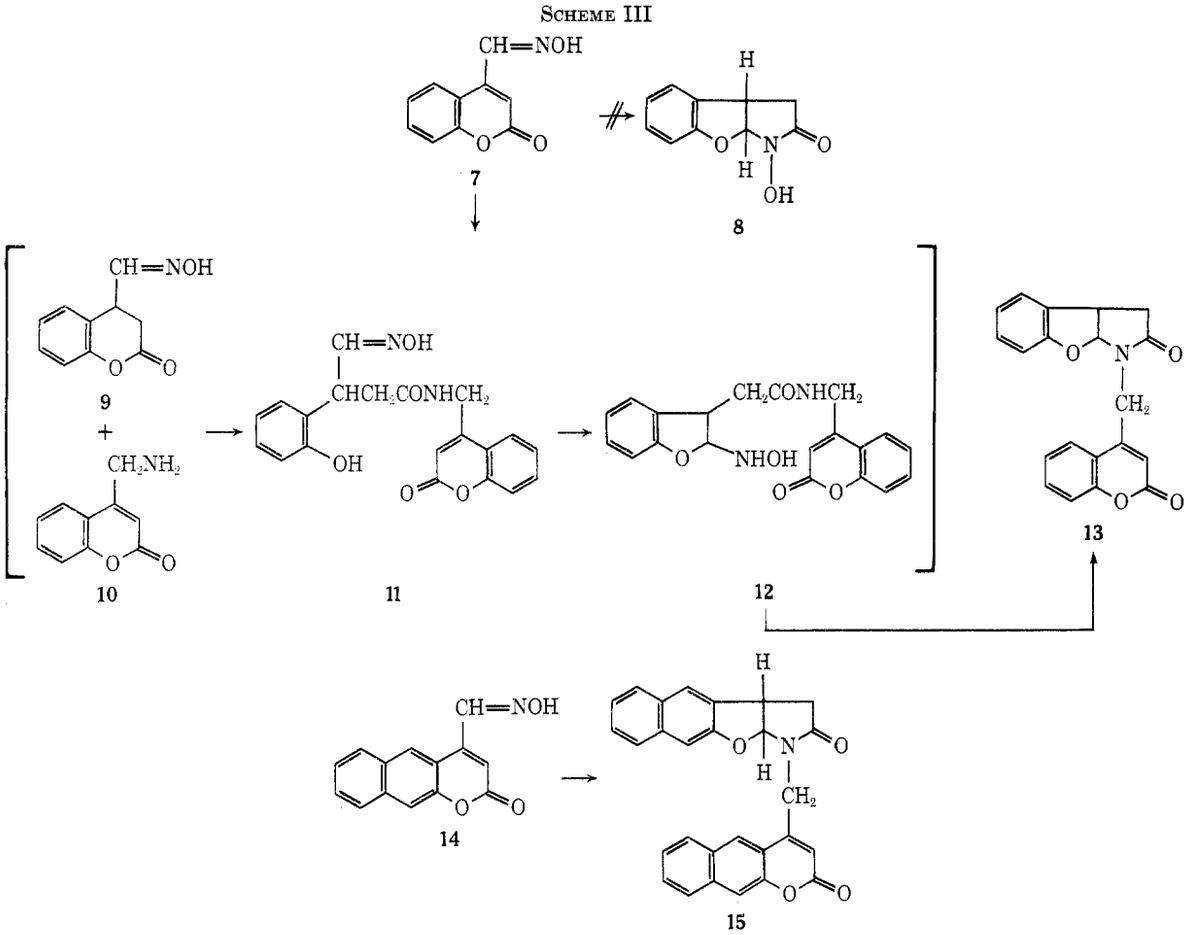
Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.96; H, 5.47; N, 5.14.

General Procedure for the Preparation of Oximes.—A mixture of 4-formylcoumarin (0.03 mol), hydroxylamine hydrochloride (0.03 mol), sodium acetate (1 g), water (5 ml), and 95% ethanol (50 ml) was refluxed for 5 hr, cooled, and poured onto ice. The white, crystalline solid which precipitated was filtered and washed with water.

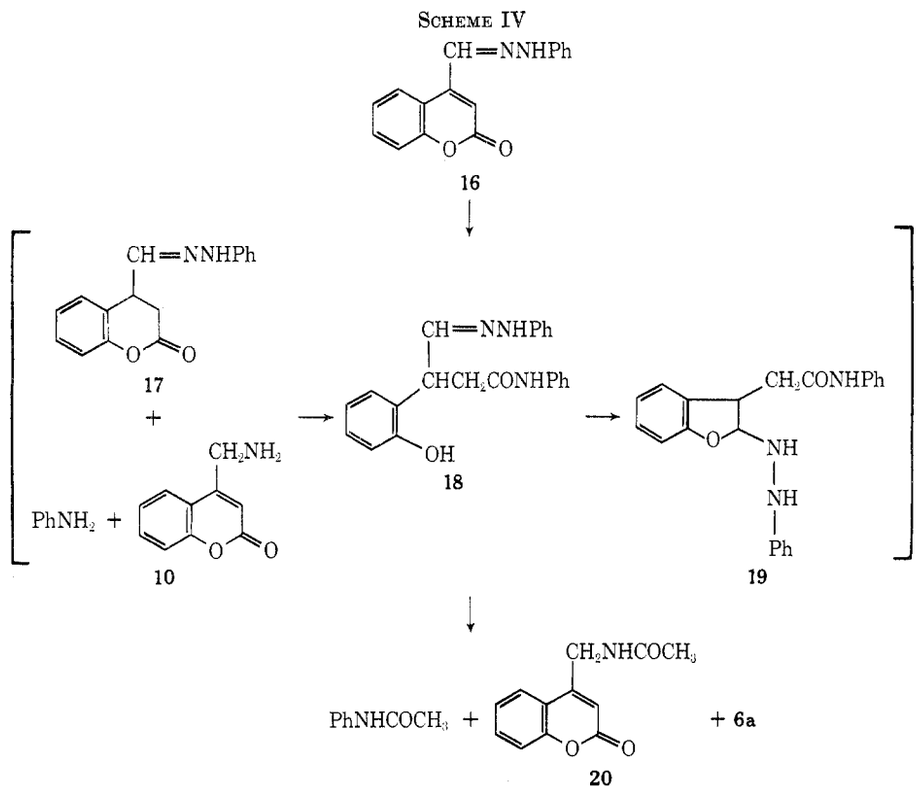
4-Formylcoumarin Oxime (7).—White crystals were recrystallized from ethyl acetate–methanol to give **7** (77%): mp 246–248°; λ_{max}^{EtOH} 232 mμ (ε 1400), 284 (12,000); ν_{max}^{Nujol} 1700 cm^{-1} (lactone C=O); nmr (DMSO-d_6) δ 12.40 (s, broad, 1, OH, exchanges with D_2O), 8.50 (s, 1, HC=N), 8.41 (d, 1, J = 6 Hz, C_5 H), 7.70–7.15 (m, 3, ArH), and 6.26 (s, 1, C_3 H).

(8) The reduction of 6-chloro-4-formylcarbostyril with zinc and acetic acid yielded 6-chloro-4-(hydroxymethyl)carbostyril as the sole product.

SCHEME III



SCHEME IV



Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.40. Found: C, 63.71; H, 3.71; N, 7.17.

β-Formyl-3-hydroxy-2-naphthaleneacrylic Acid δ-Lactone Oxime (14).—Yellow crystals were recrystallized from DMF to give 14 (80%): mp 255–256°; λ_{max}^{EtOH} 232 mμ (ε 40,000), 277 (16,000), 330 (12,000); ν_{max}^{Nujol} 1700 cm^{-1} (lactone C=O); nmr (DMSO-d_6) δ 12.75 (s, broad, 1, OH, exchanges with D_2O), 9.20 (s, 1), 8.83 (s, 1), 8.35–7.50 (m, 5, ArH), and 6.85 (s, 1, C_3 H).

Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86. Found: C, 70.15; H, 3.90; N, 5.43.

4-Formylcoumarin Phenylhydrazone (16).—A mixture of 4-formylcoumarin (5.22 g, 0.03 mol), phenylhydrazine hydrochloride (4.32 g, 0.03 mol), sodium acetate (2 g), water (30 ml), and dioxane (60 ml) was warmed on a steam bath for 1 hr. The reaction mixture was cooled. The crystalline precipitate which formed was filtered and recrystallized from methanol to give orange crystals (5 g, 64%): mp 196–198°; λ_{max}^{EtOH} 260 mμ (ε 13,000), 410 (22,500); ν_{max}^{Nujol} 1720 cm^{-1} (lactone C=O); nmr (DMSO-d_6) δ 11.20 (s, 1, NH exchanges with D_2O), 8.58 (d, 1, J = 9 Hz, C_5 H), 8.10 (s, 1, HC=N), 7.65–7.00 (m, 8, ArH), and 6.60 (s, 1, C_3 H).

Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; 4.58; N, 10.60. Found: C, 72.62; H, 4.45; N, 10.78.

4-Formylcoumarin Semicarbazone.—A solution of semicarbazide hydrochloride (1.11 g, 0.01 mol) in water (5 ml) was added to a solution of 4-formylcoumarin (1.74 g, 0.01 mol) in dioxane (20 ml). The resulting mixture was warmed on a steam bath for 30 min. The precipitate which formed was filtered, washed with water, and recrystallized from DMF to give white crystals (1.3 g, 56%): mp 247–249°; ν_{max}^{Nujol} 1720, 1710, and 1690 cm^{-1}; nmr (DMSO-d_6) δ 10.67 (s, 1, NH, exchanges with D_2O), 8.16 (s, 1, HC=N), 8.07 (d, 1, J = 10 Hz, C_5 H), 7.65–7.00 (m, 3, ArH), 6.83 (s, 1, C_3 H), and 6.60 (s, 2, NH_2 exchanges with D_2O).

Anal. Calcd for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 56.87; H, 4.00; N, 18.09.

General Procedure for the Rearrangements.—Zinc dust was added to a solution of the substrate (0.03 mol) in glacial acetic acid (100 ml) at 100°. The reaction mixture was stirred at this temperature for 2 hr, cooled, diluted with chloroform, filtered, and concentrated. The crude oil obtained was dissolved in chloroform. The resulting solution was washed with water, dried over $MgSO_4$, and evaporated to give a colorless gum, which crystallized on standing.

3a,8a-Dihydrofuro[2,3-*b*]benzofuran-2(3*H*)-one (2).—White crystals were recrystallized from methanol to give **2** (36%): mp 124–126°; λ_{max}^{EtOH} 274 mμ (ε 2600), 281 (2200); ν_{max}^{Nujol} 1780 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.30–6.70 (m, 4, ArH), 6.42 (d, 1, J = 6 Hz, C_{8a} H), 4.17 (m, 1, C_{3a} H), 2.94 (d, 1, J = 9 Hz, C_3 H), and 2.80 (d, 1, J = 3 Hz, C_3 H).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.06; H, 4.54.

3a,10a-Dihydronaphtho[2′,3′:4,5]furo[2,3-*b*]furan-2(3*H*)-one (4).—White crystals were recrystallized from ethyl acetate to give **4** (55%): mp 224–226°; λ_{max}^{EtOH} 264 mμ (ε 4500), 274 (5000), 285 (3500), 316 (2000), 329 (3000); ν_{max}^{Nujol} 1780 cm^{-1} (C=O); nmr (DMSO-d_6) δ 7.85–7.10 (m, 6, ArH), 6.64 (d, 1, J = 6 Hz, C_{10a} H), 4.30 (m, 1, C_{3a} H), 3.18 (d, 1, J = 9 Hz, C_3 H), and 2.90 (d, 1, J = 3 Hz, C_3 H).

Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.06; H, 4.40.

1-Phenyl-1,3,3a,8a-tetrahydro-2*H*-benzofuro[2,3-*b*]pyrrol-2-one (6a).—White crystals were recrystallized from ethyl acetate to give **6a** (50%): mp 105–107°; λ_{max}^{EtOH} 276 mμ (ε 4800), 284 (4400); ν_{max}^{Nujol} 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.80–6.65 (m, 9, ArH), 6.37 (d, 1, J = 8 Hz, C_{3a} H), 4.05 (m, 1, C_{3a} H), 2.95 (d, 1, J = 9 Hz, C_3 H), and 2.80 (d, 1, J = 4 Hz, C_3 H).

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.26; H, 5.30; N, 5.60.

1-(3,4-Dimethylphenyl)-1,3,3a,8a-tetrahydro-2*H*-benzofuro-[2,3-*b*]pyrrol-2-one (6b).—White crystals were recrystallized from ethyl acetate to give **6b** (46%): mp 109–111°; λ_{max}^{EtOH} 276 mμ (ε 4800), 284 (4000); ν_{max}^{Nujol} 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.80–6.65 (m, 7, ArH), 6.30 (d, 1, J = 7 Hz, C_{3a} H), 4.00 (m, 1, C_{3a} H), 2.88 (d, 1, J = 9 Hz, C_3 H), 2.73 (d, 1, J = 3 Hz, C_3 H), and 2.30 (s, 6, $-CH_3$).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.24; H, 6.10; N, 5.06.

1-[(2-Oxo-2*H*-1-benzopyran-4-yl)methyl]-1,3,3a,8a-tetrahydro-2*H*-benzofuro[2,3-*b*]pyrrol-2-one (13).—White crystals were recrystallized from ethyl acetate to give **13** (57%): mp 90–93°; λ_{max}^{EtOH} 275 mμ (ε 11,200), 312 (5200); ν_{max}^{Nujol} 1720 (lactone C=O), 1695 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 7.90–6.65 (m, 8, ArH), 6.23 (s, 1, =CH), 6.00 (d, 1, J = 8 Hz, C_{3a} H), 4.78 (s, 1, NCH_2–), 4.55 (s, 1, NCH_2–), 4.00 (m, 1, C_{3a} H), 2.92 (d, 1, J = 9 Hz, C_3 H), and 2.78 (d, 1, J = 3 Hz, C_3 H); mass spectrum (70 eV) m/e 333 (100), 174 (38), 160 (38), 131 (75).

Anal. Calcd for $C_{20}H_{15}NO_4$: C, 72.06; H, 4.54; N, 4.20. Found: C, 71.88; H, 4.78; N, 4.03.

1-[(2-Oxo-2*H*-naphtho[2,3-*b*]pyran-4-yl)methyl]-1,3,3a,10a-tetrahydro-2*H*-naphtho[2′,3′:4,5]furo[2,3-*b*]pyrrol-2-one (15).—White crystals were recrystallized from DMF to give **15** (73%): mp 263–265°; ν_{max}^{Nujol} 1725 (lactone C=O), 1694 cm^{-1} (amide C=O).

Anal. Calcd for $C_{28}H_{19}NO_4$: C, 77.58; H, 4.42; N, 3.23. Found: C, 77.40; H, 4.46; N, 3.42.

4-[(Acetamido)methyl]coumarin (20).—White crystals were recrystallized from methanol to give **20** (6%): mp 185–186°; ν_{max}^{Nujol} 1710 (lactone C=O), 1665 cm^{-1} (amide C=O); nmr (DMSO-d_6) δ 9.00 (t, 1, J = 6 Hz, NH exchanges with D_2O), 8.10–7.20 (m, 4, ArH), 6.35 (s, 1, C_3 H), 4.60 (d, 2, J = 6 Hz, $-CH_2N$, s after D_2O exchange), and 2.01 (s, 3, CH_3–).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.32; H, 5.28; N, 6.24.

Acknowledgment.—We would like to express our gratitude to Dr. R. C. Greenough for the spectral data and Mrs. U. Zeek for the elemental analyses.

Registry No.—**1**, 35893-95-9; 1 semicarbazone, 41594-38-1; **2**, 41594-39-2; **3**, 41594-40-5; **4**, 41594-41-6; **5a**, 41594-42-7; **5b**, 41594-43-8; **6a**, 41594-44-9; **6b**, 41594-45-0; **7**, 41594-46-1; **13**, 41594-47-2; **14**, 41594-48-3; **15**, 41594-49-4; **16**, 41594-50-7; **20**, 41594-51-8; aniline, 62-53-3; 3,4-xylidine, 95-64-7.