Pyrimidines. 18. A Novel Pyrimidine to Benzene Ring Transformation Reaction. Conversion of 5-Nitro-2(1*H*)-pyrimidinone into *p*-Nitrophenol Derivatives

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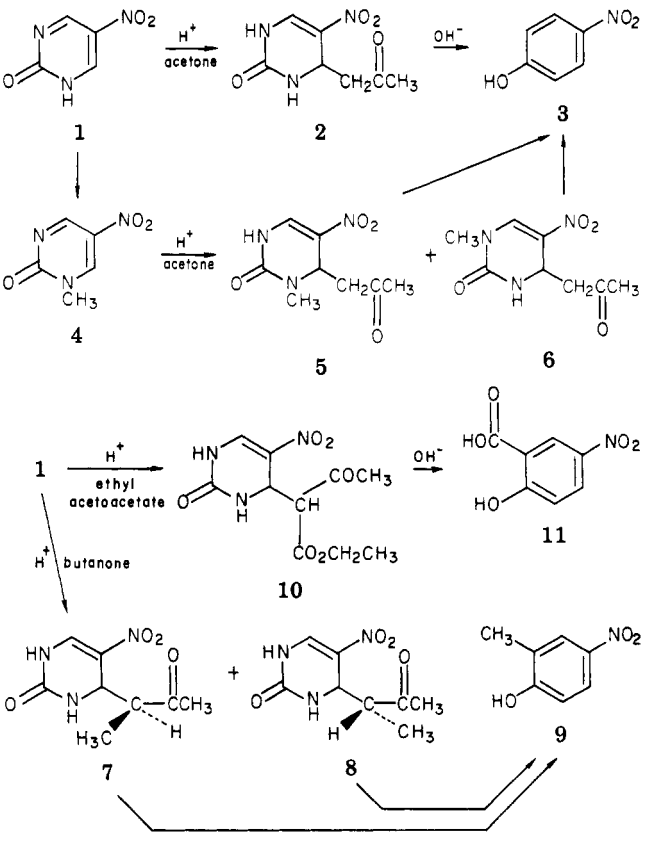
5-Nitro-2(1*H*)-pyrimidinone (1) underwent acid-catalyzed condensation with acetone and ethyl acetoacetate to form 4-ketonyl-5-nitropyrimidines **2** and **10** which were readily converted into *p*-nitrophenol (**3**) and 5-nitrosalicyclic acid (**11**), respectively, by NaOH treatment. Condensation of **1** with butanone gave a pair of diastereomeric adducts **7** and **8**. Upon base treatment both **7** and **8** afforded 4-nitrocresol (**9**). Acid-catalyzed reaction of **1** with diethyl acetonedicarboxylate led to the formation of a [3.3.1] bicyclic adduct **12** which underwent base-catalyzed conversion into 2-hydroxy-5-nitroisophthalic acid (**13**). Treatment of 1-methyl-5-nitro-2(1*H*)-pyrimidinone (**4**) with acetone in the presence of acid afforded 4-acetonyl-3-methyl (**5**) and 4-acetonyl-1-methyl (**6**) adducts which were converted separately into **8**. Identification and characterization of the ketonyl adducts are reported. Mechanisms of overall conversions of **1** and **4** into the *p*-nitrophenol derivatives are offered.

A number of reports have appeared concerning the conversion of nitrogen-containing monocyclic derivatives into other heterocyclic ring systems.[2] Thus, the *s*-triazine system has been converted into pyrimidine[3-7] or pyridine[5,6] rings, and pyrimidine derivatives into pyridines[7-10] or pyridopyrimidines.[11-13] Pyrimidine to benzene ring transformation, however, has not been known until very recently.[14,15] Barczynski and van der Plas[14a] reported that 5-nitropyrimidine was converted into either the 3-nitropyridine derivative, the 4-nitrophenol, or 4-pyridone by treatment with ketonic reagents. On the other hand, treatment of 5-nitropyrimidine with amidines afforded only 5-nitropyridine derivatives.[14b] Hirota et al.[15] obtained the 4-hydroxybenzoic acid esters from the reaction mixture of 5-formyl-1,3-dimethyluracil with acetonylacetone derivatives in base.

During the course of studies aimed at synthesis of inhibitors of enzymes involved in pyrimidine metabolism, we found an interesting intermolecular pyrimidine to benzene transformation reaction.[16] 5-Nitro-2(1*H*)-pyrimidone (**1**) underwent an acid-catalyzed addition reaction with acetone to form a crystalline adduct in quantitative yield (Scheme I). The structure of the adduct was established as 4-acetonyl-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (**2**) on the basis of its spectral characteristics. The UV spectrum at neutral pH showed an absorption maximum at 353 nm (ϵ 9000), which indicated a vicinal amino-nitro olefin system in the molecule.[17] The ^{1}H NMR spectrum of this adduct in deuterated dimethyl sulfoxide (Me_2SO-d_6) showed the presence of a methyl singlet at δ 2.12, a deformed doublet for a methylene at δ 2.87, an aliphatic proton multiplet at δ 4.83, an olefinic doublet

Scheme I



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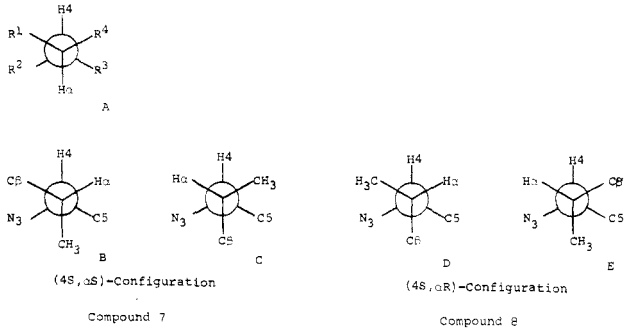

Figure 1. The Newman projection of 4-(butan-2-on-3-yl)-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidines along the Cα–C4 bond. Mirror images corresponding to B and C (4*R*,α*R*) and D and E (4*R*,α*S*) are not shown.

integrated for one proton at δ 8.00, and two dissociable (NH) proton signals at δ 7.55 and 9.90. The signals at δ 4.83 and 8.00 became a triplet and a singlet, respectively, upon exchange of the NH protons by deuterium. These spectral data of the adduct, as well as the elemental analyses, are consistent with structure **2**.

Compound **2** was converted very easily into *p*-nitrophenol (**3**) under alkaline conditions. The UV absorption spectrum of **2** in an alkaline solution underwent both bathochromic and hyperchromic change as a function of time. The final curve exhibited a maximum at 400 nm, which upon acidification shifted the maximum to 315 nm. The shift was reversible. These UV absorption characteristics were identical with those of *p*-nitrophenol,[18] indicating that 2 underwent transformation. From the acidified solution, *p*-nitrophenol was isolated in almost quantitative yield.

Treatment of 1-methyl-5-nitro-2(1*H*)-pyrimidone (**4**) with acetone in the presence of acid afforded a mixture which was separated by fractional crystallization into two compounds. 4-Acetonyl-3-methyl-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (**5**), mp 158.8–159.4 °C (UV λ_{max} 358 nm), and 4-acetonyl-1-methyl-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (**6**), mp 166.5–167.2 °C (UV λ_{max} 370 nm). These structures were established by ^{1}H NMR (Me_2SO-d_6). The signal for H4 of compound **5** at δ 4.95 was a triplet, whereas the H4 signal for **6** was a multiplet which collapsed to a triplet upon replacement of the NH proton with deuterium. These results showed clearly that the acetonyl products were formed by addition of acetone to 5-nitropyrimidones by both the 1,2 and 1,4 fashion. Both **5** and **6** were converted smoothly into *p*-nitrophenol under alkaline conditions with elimination of *N*-methylurea.

Acid-catalyzed condensation of **1** with 2-butanone gives a mixture of two racemates **7** and **8**. Both racemates were separated in crystalline form. A comparison of their ^{1}H NMR spectra revealed that only the H4 signals in these racemates are significantly different in chemical shifts (δ 5.12 and 4.92, respectively). The rather small coupling between H4 and Hα in **7** and **8** ($J_{4,\alpha} \simeq$ 2.2 and 2.7 Hz, respectively) ruled out the trans configuration between H4 and Hα (A, Figure 1). Since the chemical shifts of all the corresponding nondissociable protons are very close (largest $\Delta\delta \simeq$ 0.06 Hz), the relative dispositions between the methyl group attached to Cα and the nitro group on C5 in both **7** and **8** should be very similar. The possibility of D and its mirror image could therefore be eliminated. The Hα signal is expected to shift to a lower field when Hα comes close to the nitro group on C5. Thus, compound **7** (Hα at δ 5.12) is most likely to be B and its mirror image

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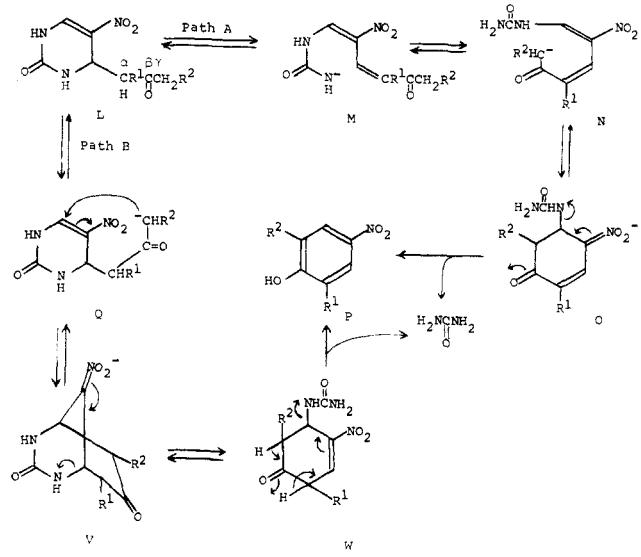

Figure 2. Mechanisms of pyrimidine to benzene ring transformation.

and compound **8** (Hα at δ 4.92) to be E and its mirror image. The fact that both **7** and **8** were converted into 4-nitrocresol (**9**) by treatment with sodium hydroxide is consistent with structures B and E and their corresponding mirror images.

When **1** was treated with ethyl acetoacetate in the presence of an acid catalyst, a single racemate, ethyl 2-(2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidin-4-yl)acetoacetate (**10**), was obtained. This racemate showed two methyl signals (a singlet at δ 2.23 for $COCH_3$ and a triplet at δ 1.17 for CH_2CH_3) in the ^{1}H NMR spectrum. Base-catalyzed ring transformation of **10** followed by acidification afforded 5-nitrosalicyclic acid (**11**).

Reaction of **1** with diethyl acetonedicarboxylate in acid afforded a crystalline product. The UV absorption maximum of this product was at 252 nm (not at 350–360 nm), indicating the absence of the vicinal amino-nitro olefin system in the molecule. In the ^{1}H NMR spectrum (Me_2SO-d_6), three signals integrated for one proton each at δ 5.17, 4.78, and 4.50 are observed. In addition, there are four exchangeable proton signals at δ 12.0, 7.33, 6.49, and 3.67 and a pair of slightly nonequivalent ethyl signals, but no olefinic proton signal was found in the ^{1}H NMR spectrum. These data suggest that the product has the 2,4-diazabicyclo[3.3.1]nonene system **12**. The low (δ 12.0) and high (δ 3.67) field exchangeable proton signals are assigned to the enolic proton[20] and H8, respectively, and two other signals at δ 7.33 and 6.94 to two NH protons. Three remaining signals are observed that correspond to H1, H5, and H9. Compound **12** was converted into 2-hydroxy-5-nitroisophthalic acid (**13**) by base-catalyzed ring transformation reaction.

Conversion of the ketone–nitropyrimidinone adducts ([L], Figure 2) into nitrophenols [P] may proceed by the following two mechanisms, depending upon the relative acidity between the α and γ carbons in [L]. When the α carbon is more acidic than γ, path A Figure 2) would operate predominantly. Dissociation of the proton from the α-carbon would cause ring opening between N3 and C4 to form intermediate [M]. Dissociation of the proton at γ position from M in base would result in the formation

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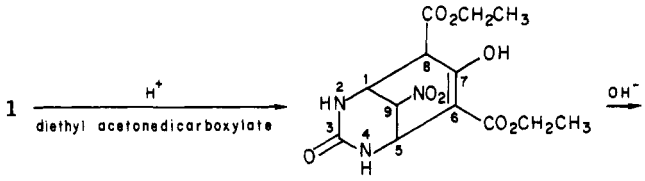

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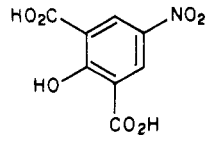

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of carbanion [N]. Cyclization between the carbanion and C6 by assistance from the nitro group would lead to the formation of *aci*-nitro intermediate [O] from which *p*-nitrophenol products [P] would arise by simultaneous elimination of urea and aromatization.

If the proton on Cγ is more labile than that on Cα, path B should predominate. In this case, the initial step is abstraction of a proton from Cγ of [L] to give the carbanion [Q], which should then undergo intramolecular cyclization leading to formation of the Michael addition product [V]. This intermediate [V] is structurally very similar to the bicyclic derivative **12**, obtained by acid-catalyzed condensation of **1** with diethyl acetonedicarboxylate. Conversion of [V] into the *p*-nitrophenol product [P] would proceed via the ureido intermediate [W].

It is interesting to note that σ-complex formation is not involved in our pyrimidine to benzene transformation reactions. It is known that stable σ complexes are formed by base-catalyzed reaction of 5-nitropyrimidines with ketonic reagents such as acetone and acetophenone.[21,22] Also, σ complex plays the key role as intermediate in the ring transformation of 5-nitropyrimidine into pyridine and benzene derivatives reported by Baczynski and van der Plas.[14]

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian A-60 or JEOL PFT-100 spectrometer using Me_2SO-d_6 as the solvent with Me_4Si as the internal standard. Chemical shifts are reported in parts per million (δ) and signals are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), and dq (double quartet). Values given for coupling constants are first order. UV absorption spectral data were determined on a Cary Model 15 spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Spang Microanalytical Laboratory, Eagle Harbor, MI.

4-Acetonyl-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (2). A solution of 5-nitro-2(1*H*)-pyrimidinone[23] (1.41 g, 10 mmol) in acetone (100 mL) containing one drop of 1 N HCl was gently refluxed for 5 h. The yellow solution was concentrated in vacuo, and the residue was recrystallized from ethanol. The yield of **2** was 1.62 g (82%): mp 173–174 °C; UV (H_2O) λ_{max} 233 nm (ε 4830), 248 (4850), 351 (10 200), λ_{min} 240 (4790), 286 (2410); ^{1}H NMR δ 2.10 (3 H, s, $COCH_3$), 2.82 (2 H, m, CH_2), 4.85 (1 H, m, H4), 7.63 (1 H, d, 3 H, exchangeable), 7.99 (1 H, s, H6), 9.94 (1 H, br, 1 NH exchangeable).

Anal. Calcd for $C_7H_9N_3O_4$: C, 42.21; H, 4.55; N, 21.10. Found: C, 42.19; H, 4.55; N, 21.12.

1-Methyl-5-nitro-2(1*H*)-pyrimidinone (4). A mixture of **1** (1.41 g, 10 mmol), powdered KOH (0.56 g, 10 mmol), and methyl iodide (1 mL, 16 mmol) was heated at reflux for 3 h. The mixture was concentrated in vacuo, and the residue was extracted with benzene in a Soxhlet. The benzene extracts were concentrated in vacuo, and the residue was recrystallized from benzene to give 1.10 g (71%) of **4**: mp 169–170 °C; UV (H_2O) λ_{max} 316 nm (ε 10 100).[24]

Anal. Calcd for $C_5H_5N_3O_3$: C, 38.72; H, 3.25; N, 27.09. Found: C, 38.91; H, 3.48; N, 27.07.

Treatment of 4 with Acetone. A solution of **4** (1.0 g, 6.5 mmol) in acetone (100 Ml) containing one drop of 1 N HCl was gently refluxed overnight. The yellow solution (λ_{max} 365 nm) was concentrated in vacuo to a yellow solid (1.35 g, 98%, mp 130–170 °C), which was triturated at room temperature with 5-mL portions of ethanol. After filtration, each extract was concentrated in vacuo to dryness. The first two crops (150 mg) contained a yellow, oily contaminant and were set aside. The following six crops of pale yellow needles (the yields steadily diminished from 80 to 25 mg) were combined (260 mg) and recrystallized from benzene. **Pure 4-acetonyl-3-methyl-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (5)** was obtained as pale yellow needles: 190 mg, mp 159–159.5 °C; UV (H_2O) λ_{max} 253 nm (ε 3740), 358 (8070), λ_{min} 295 (2180); ^{1}H NMR (Me_2SO-d_6) δ 2.12 (3 H, s, $COCH_3$), 2.93 (2 H, d, CH_2), 2.83 (3 H, s, NCH_3), 4.95 (1 H, t, H4), 7.97 (1 H, d, H6), 10.07 (1 H, br, exchangeable, 1 NH).

The unextracted crystalline residue (900 mg) was recrystallized from ethanol to afford **4-acetonyl-1-methyl-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (6)** as yellow prisms: mp 166.5–167.2 °C; UV (H_2O) λ_{max} 245 nm (ε 4620), 370 (10 460) λ_{min} 293 (1300); ^{1}H NMR δ 2.12 (3 H, s, $COCH_3$), 2.85 (2 H, d, CH_2), 3.17 (3 H, s, NCH_3), 4.88 (1 H, m, H4), 7.65 (1 H, br, 3 NH, exchangeable), 8.33 (1 H, s, H6).

Anal. Calcd for $C_8H_{11}N_3O_4$: C, 45.07; H, 5.20; N, 19.71. Found for **5**: C, 45.10; H, 5.50; N, 19.31. Found for **6**: C, 45.44; H, 5.51; N, 19.30.

Treatment of 1 with Butanone. A solution of **1** (1.41 g, 10 mmol) in butanone (100 mL) containing two drops of 1 N HCl was heated at reflux for 2 h. The solvent was removed in vacuo, and the residue was twice crystallized from ethanol to give **(4*S*,α*S*)- and (4*R*,α*R*)-4-(butan-2-on-3-yl)-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (7)**: 980 mg (46%), mp 242–243 °C dec; UV (H_2O) λ_{max} 233 nm (ε 4500), 248 (4540), 350 (9680), λ_{min} 240 (4460), 287 (2450); ^{1}H NMR δ 0.97 (3 H, d, $CHCH_3$), 2.19 (3 H, s, $COCH_3$), 2.92 (1 H, dq, $CHCH_3$), 5.12 (1 H, dd, H4), 7.53 (1 H, d, 3 NH, exchangeable), 8.08 (1 H, s, H6), 9.93 (1 H, br, 1 NH, exchangeable).

The mother liquors of crystallization were combined and evaporated in vacuo. The residue was twice recrystallized from acetonitrile to give **(4*R*,α*S*)- and (4*S*,α*R*)-4-(butan-2-on-3-yl)-2-oxo-1,2,3,4-tetrahydro-5-nitropyrimidine (8)**: 639 mg (30%), mp 170–172 °C dec; UV (H_2O) λ_{max} 233 nm (ε 4500), 248 (4540), 350 (9670), λ_{min} 240 (4460), 287 (2450); ^{1}H NMR δ 0.97 (3 H, d, $CHCH_3$), 2.14 (3 H, s, $COCH_3$), 2.86 (1 H, dq, $CHCH_3$), 4.92 (1 H, dd, H-4), 7.91 (1 H, d, 3 NH, exchangeable, $J_{NH,3}$ = 3.0 Hz), 8.05 (1 H, s, H6), 9.95 (1 H, br, 1 NH, exchangeable).

Anal. Calcd for $C_8H_{11}N_3O_4$: C, 45.07; H, 5.20; N, 19.71. Found for **7**: C, 45.04; H, 5.26; N, 19.67. Found for **8**: C, 44.97; H, 5.27; N, 19.51.

Ethyl 2-(2-Oxo-1,2,3,4-tetrahydro-5-nitropyrimidin-4-yl)-acetoacetate (10). A mixture of **1** (1.41 g, 10 mmol) and ethyl acetoacetate (2.5 g, 20 mmol) in 95% ethanol (30 mL) containing two drops of 1 N HCl was heated at reflux for 5 h. After removal of the solvent in vacuo, the residue was crystallized from ethanol to give 1.66 g (61%) of **10**: mp 153–154 °C; UV (H_2O) λ_{max} 228 nm (ε 4370), 326 (11 400), λ_{min} 244 (3520); ^{1}H NMR δ 1.17 (3 H, t, CH_2CH_3), 2.23 (3 H, s, $COCH_3$), 4.00 (1 H, d, Hα, $J_{4,\alpha}$ = 3.0 Hz), 4.09 (2 H, q, CH_2CH_3), 5.25 (1 H, t, H4), 7.60 (1 H, br, 3 NH, exchangeable), 8.07 (1 H, d, H6), 10.1 (1 H, br, 1 NH, exchangeable).

Anal. Calcd for $C_{10}H_{13}N_3O_6$: C, 44.28; H, 4.83; N, 15.49. Found: C, 44.31; H, 4.90; N, 15.69.

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Diethyl 9-Nitro-3-oxo-2,4-diazabicyclo[3.3.1]non-6-ene-6,8-dicarboxylate (12). A mixture of 1 (1.41 g, 10 mmol) and diethyl 1,3-acetonedicarboxylate (2.02 g, 15 mmol) in 95% ethanol (30 mL) containing two drops of 1 N HCl was heated at reflux for 30 h. The solvent was removed in vacuo and the residue was chromatographed over a column of silica gel (Woelm 70-230 mesh, 30 × 3 cm), using chloroform as the eluent. From the major UV absorbing fraction, 1.37 g (40%) of **12** was obtained: mp 149-150 °C dec; UV (H_2O) λ_{max} 252 nm (ϵ 7210); ^1H NMR δ 1.21 (3 H, t, CH_2CH_3), 1.31 (3 H, t, CH_2CH_3), 3.67 (1 H, d, H8, exchangeable, $J_{1,8}$ = 2.1 Hz), 4.16 (2 H, q, CH_2CH_3), 4.19 (2 H, q, CH_2CH_3), 4.50 (1 H, m, H1), 4.78 (1 H, m, H5) 5.17 (1 H, narrow m, H9), 6.94 (1 H, d, NH, exchangeable), 7.33 (1 H, d, NH, exchangeable), 12.0 (1 H, s, enolic OH, exchangeable).

Anal. Calcd for $C_{13}H_{17}N_3O_8 \cdot 0.5H_2O$: C, 44.32; H, 5.15; N, 11.93. Found: C, 44.55; H, 4.98; N, 12.04.

***p*-Nitrophenol (3) from Compound 2.** A solution of **2** (200 mg, 1 mmol) in 1 N NaOH (30 mL) was stirred at room temperature for 5 h. The dark-yellow solution was cooled in an ice bath and then acidified with 6 N HCl to pH ~2. The solution was extracted with ether (3 × 40 mL). The ether extracts were dried and evaporated, and the residue was crystallized from water to give 118 mg (85%) of **3**, mp 112-113 °C. A mixture of this material with an authentic sample showed no depression of the melting point. The IR and UV absorption spectra were identical in every detail with that of an authentic sample.

In a similar manner, **3** was obtained from **5** and **6** in quantitative yield. Compounds **7** and **8** were converted into 4-nitrocresol **9**: mp 93-94 °C (lit.[25] mp 93-94 °C); UV λ_{max} 229 nm (ϵ 6600), 325 (9200), λ_{min} 257 (1000); ^1H NMR δ 2.20 (3 H, s, CH_3), 6.94 (1 H, s, H6), 7.93 (1 H, dd, H5), 8.03 (1 H, d, H3).

Anal. Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.97; H, 4.64; N, 8.99.

5-Nitrosalicylic Acid (11) from Adduct 10. A solution of **10** (259 mg, 1 mmol) in 1 N NaOH (30 mL) was stirred for 5 h at room temperature. Upon acidification of the mixture with 6 N HCl to pH ~2, 5-nitrosalicylic acid (**11**) precipitated. Recrystallization of the precipitate from water gave pure **11**: 130 mg (70%), mp 228-229 °C (lit.[26] mp 228-229 °C); UV λ_{max} 219 nm (ϵ 13500), 250 (sh) (4500), 315 (9500), λ_{min} 268 (2600); ^1H NMR δ 7.16 (1 H, d, H3, $J_{3,4}$ = 9.2 Hz), 8.34 (1 H, dd, H4, $J_{3,4}$ = 9.2, $J_{4,6}$ = 2.8 Hz), 8.57 (1 H, d, H6, $J_{4,6}$ = 2.8 Hz).

Anal. Calcd for $C_7H_5NO_5$: C, 45.91; H, 2.75; N, 7.65. Found: C, 45.99; H, 2.84; N, 7.63.

In a similar manner, 2-hydroxy-5-nitroisophthalic acid (**13**) was prepared from **12**, 138 mg (61%) mp 209-210 °C (lit.mp 213-214 °C); UV λ_{max} 216 nm (ϵ 17600), 325 (14700), λ_{min} 274 (3900); ^1H NMR δ 8.68 (s, H4, 6).

Anal. Calcd for $C_8H_5NO_7$: C, 42.31; H, 2.22; N, 6.17. Found: C, 42.45; H, 2.36; N, 6.38.

Registry No. 1, 23938-66-1; 2, 79918-37-9; 3, 100-02-7; 4, 17758-39-3; 5, 79918-38-0; 6, 79918-39-1; 7, 79918-40-4; 8, 79918-41-5; 9, 99-53-6; 10, 79918-42-6; 11, 96-97-9; 12, 79918-43-7; 13, 67294-53-5.

(25) *Beilstein* **1923**, *6*, 336.
(26) *Beilstein* **1927**, *10*, 116.
(27) *Beilstein* **1927**, *10*, 502.

Intramolecular Diels-Alder Cycloadditions of Perchloro(allyloxy)- and Perchlorobis(allyloxy)cyclopentadienes[1]

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The intramolecular cycloadditions of some mono(allyloxy)- and bis(allyloxy)perchlorocyclopentadienes have been carried out. Even in the case of trisubstituted olefins, this internal cycloaddition process occurs in good yield. The allyloxy compounds (**10**, **11**, **15**, and **16**) were prepared by treating hexachlorocyclopentadiene (**9**) with the corresponding allylic alcohol in basic solution. In only one case could the intermediate allyloxy diene be isolated (compound **16**), the normal process being an in situ internal Diels-Alder reaction to produce the bridged cycloadducts (**12**, **13**, **17**, and **18**) in good yield. The structures of the adducts were determined by a combination of chemical and spectroscopic means. Acidic hydrolysis of the adducts **13** and **18** produced the corresponding hydroxy ketones **8** and **19**, respectively, in high yield. NMR analysis of the adducts also confirmed the assigned structures. By the use of double-resonance and nuclear Overhauser effects, nearly all of the resonances could be assigned and the coupling constants determined. Finally, an unsuccessful attempt to apply these results to the total synthesis of the sesquiterpene β-cuparenone (**4**) is also described.

We have recently reported on the usefulness of dimethoxytetrachlorocyclopentadiene (**1**) in Diels-Alder reactions with both electron-rich and electron-poor dienophiles in a three-carbon annulation process.[3] The adducts could also serve as substrates for anionic oxy-Cope rearrangements[4] with aromatic systems in the preparation of steroid analogues[5] and in the total synthesis of coronafacic acid.[6] However, although this diene **1** is quite reactive with mono- and disubstituted olefins as dienophiles, it is very unreactive when the dienophile is tri- or tetrasubstituted. For example, the cycloaddition of **1** with isobutenyl acetate (**2**) required refluxing in neat **2** (bp 131 °C) for 3-4 weeks.[7] The adducts **3**, which could be taken on to β-cuparenone (**4**), were formed in only 38% yield in the cycloaddition process.[7] Because of these very severe conditions necessary to effect a reaction between the diene **1** and a trisubstituted olefin and because of the poor yields of adducts obtained, it was decided to investigate the possibility of performing intramolecular Diels-Alder reactions on 5-monosubstituted and 5,5-disubstituted per-

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