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Reactions of 2-Methyl-2*H*-cyclopenta[*d*]pyridazines with Nitration Reagents, Mercuric Acetate, and Tetracyanoethene[1,2]

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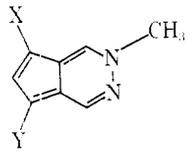
Received September 14, 1977

Azulene readily underwent mononitration on reaction with cupric nitrate and acetic anhydride,[5] tetranitromethane,[6] or nitric acid and acetic anhydride[6] with the last reagent also effecting dinitration. Mononitration of cyclopenta[*c*]thiapyran was accomplished with tetranitromethane.[7] Studies on the reactions of 2*H*-cyclopenta[*d*]pyridazines have shown that this system is also very reactive to electrophilic acylation,[8] halogenation,[9] and diazonium coupling,[10] so it was anticipated that direct nitration would occur with difficulty.

Treatment of 2-methyl-2*H*-cyclopenta[*d*]pyridazine (1) with tetranitromethane in methanol and pyridine gave extensive decomposition, Me_2SO alone gave > 90% recovery of unchanged 1, and Me_2SO plus triethylamine gave 10% recovered 1 and 7% of a mixture. The NMR spectrum showed the major components to be the 5- and 7-nitro derivatives (2 and 3) in a ratio of 1:3. Attempts to separate pure 2 and 3 failed. Attempts to introduce the nitro group with a mixture of nitric, acetic, and sulfuric acids gave unchanged 1 at room temperature and complete decomposition when warmed. Reaction with cupric nitrate and acetic anhydride at −78 °C gave a very low yield of an impure mixture of 2 and 3 and longer periods formed a tar, as did treatment of 1 with nitronium tetrafluoroborate in acetonitrile.



1, X = Y = H
2, X = H; Y = NO_2
3, X = NO_2; Y = H
4, X = Br; Y = NO_2
5, X = NO_2; Y = Br
6, X = NO_2; Y = I
7, X = I; Y = NO_2
8, X = Y = HgOAc
9, X = C(CN)=C(CN)$_2$; Y = H
10, X = H; Y = C(CN)=C(CN)$_2$

The sole route to a pure nitro derivative of 1 found was the reaction of the 7-bromo compound with silver nitrite, a method which had been discovered with 1,3-dibromoazulene and 5,7-dichlorocyclopenta[*c*]thiapyran in earlier work.[7] In the present case a 75% yield of 3 was obtained. Attempts to achieve dinitration of 3 led to decomposition. As was found for the dibromoazulene and dichlorocyclopenta[*c*]thiapyran compounds, treatment of the 5,7-dibromo derivative of 1 with excess silver nitrite effected the substitution of only one bromine per molecule and a mixture of the 5-nitro-7-bromo (4) and 5-bromo-7-nitro (5) products (79%) was obtained. That the presence of the strongly electron-withdrawing group in 5 and 6 was responsible for the inertness of the second bromine[7] was reaffirmed by the fact that the 5-trifluoroacetyl-7-bromo compound[9] gave no reaction with silver nitrite in 30 h. The 5,7-diiodo derivative of 1 also gave a mixture of the 5-nitro-7-iodo (7) and 5-iodo-7-nitro (6) products. Attempts to separate 4 from 5 and 6 from 7 were not successful.

The reaction of 1 with mercuric chloride gave a product which appeared to be a complex of the expected 5,7-bis(chloromercuri) derivative[11] with mercuric chloride. Reaction with 2 equiv of mercuric acetate, however, gave a 65% yield of the 5,7-diacetoxymercuri compound (8). The use of excess mercuric acetate resulted in no separation of 8 from the solution, and 8 was redissolved by the reagent, again indicating complexation. An attempt to convert 8 to the 5,7-dibromo derivative by reaction with NBS gave a small amount of impure material which contained (spectral identification) the expected product.

Azulene reacts with tetracyanoethene to give the substitution product, 1-azulyltricyanoethene.[12] This mode of reaction was also found for 1 and the 7-tricyanoethenyl compound (9) was isolated in 41% yield. Also obtained was a small amount (4%) of product spectrally (NMR, IR, mass spectrum) characterized as the isomeric 5-tricyanoethenyl derivative (10). The low solubility of 9 and 10 made their separation difficult. The immediate and pronounced darkening of the color observed upon contact of 1 with tetracyanoethene was consistent with the intermediacy of a charge transfer or π complex,[13] and it is suggested that the nonsubstitution reactions of 1 with the reagents for direct nitration wherein darkening also occurred might have involved an electron transfer from 1 to the electrophilic species.

Experimental Section[14]

7-Nitro-2-methyl-2*H*-cyclopenta[*d*]pyridazine (3). A mixture of 34.5 mg (0.164 mmol) of 7-bromo-2-methyl-2*H*-cyclopenta[*d*]-pyridazine[9] and 575.7 mg (3.74 mmol) of $AgNO_2$ in 14 mL of Me_2SO was heated (steam bath) for 16 h under a N_2 atmosphere and then shaken with 50 mL of H_2O and 50 mL of CH_2Cl_2. The resultant mixture was filtered and the filtrate phases were separated. The aqueous layer was extracted with CH_2Cl_2 and the solvent was removed from the combined, washed (H_2O), dried, and filtered organic solutions. Chromatography (silica gel plate, 4:1 $HCCl_3$–ether) separated two fractions, the first of which was unchanged starting material. The second yielded 21.7 mg (75%) of 3 as yellow needles: softening and sublimation at 164–169 °C; mp 170–171 °C; NMR (acetone) δ 9.72 (s, 1, H-4), 9.18 (s, 1, H-1), 7.9 (d, 1, H-6, J = 4 Hz), 6.77 (d, 1, H-5, J = 4 Hz), and 4.60 (s, 3, N–CH_3); UV (ether) ($\epsilon \times 10^{-3}$) 243 (24), 267 (12), 272 (sh, 11), 292 (5.3), 336 (8.3), 349 (sh, 6.4), and 416 nm (11). Anal. Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.95. Found: C, 54.07; H, 4.12.

Reaction of 1 with Tetranitromethane. A solution of 3.0 mL (1.5 mmol) of 0.5 M tetranitromethane in methanol was added (30 min) to 109.3 mg (0.829 mmol) of 1 in 3 mL of Me_2SO and 0.5 mL of tri-

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ethylamine. After 5 min the mixture was poured into 100 mL of H_2O and 100 mL of CH_2Cl_2 and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 and the solvent was removed from the combined, washed (H_2O) and dried organic solutions. Chromatography (silica gel column, 50:1 CH_2Cl_2–acetone) separated a yellow-orange solid which on rechromatography (silica gel plate, CH_2Cl_2) gave two fractions. The first yielded 11.3 mg (10.3%) of unchanged **1**: mp 123–125 °C (lit.[15] 128–129 °C); UV and visible spectrum identical with those of authentic sample. The second gave 10.5 mg (7.17%) of yellow solid, mp 152–154 °C, indicated to be a 3:1 mixture of **3** and **2** by its spectra: NMR (acetone) δ 9.63 (s, 3, H-4, **3**), 9.47 (s, 1, H-4, **2**), 9.35 (s, 1, H-1, **3**), 9.08 (s, 1, H-1, **2**), 7.86 (d, 3, H-6, **3**, J = 4 Hz), 7.73 (d, 1, H-6, **2**, J = 4 Hz), 6.80 (d, 1, H-7, **2**, J = 4 Hz), 6.70 (d, 3, H-5, **2**, J = 4 Hz), 4.53 (s, 9, N-CH_3, **3**), and 4.45 ppm (s, 3, N-CH_3, **2**); UV (ether) (D_{max}) 267 (1.58), 292 (0.80), 338 (0.97), 350 (sh, 0.84) 408 (1.10), and after dilution 243 (0.77) and 267 nm (0.40).

Reaction of 5,7-Dibromo-2-methyl-2*H*-cyclopenta[*d*]pyridazine with Silver Nitrite. A mixture of 69.6 mg (0.24 mmol) of the 5,7-dibromo compound[9] and 223.5 mg (1.45 mmol) of $AgNO_2$ in 5 mL of Me_2SO was heated (steam bath) under N_2 for 48 h and then shaken with 125 mL of H_2O and 30 mL of CH_2Cl_2. The separated aqueous layer was extracted with CH_2Cl_2 and the solvent was removed from the combined, washed (H_2O), dried, and filtered organic solutions. Chromatography (silica gel column, CH_2Cl_2) of the residue separated a yellow band which yielded 48.2 mg (78.5%) of yellow solid, mp 236–238 °C dec, indicated to be a 1:1 mixture of **4** and **5** by its spectra: NMR (Me_2SO) δ, 9.85 (s, 1 H), 9.55 (s, 1 H), 9.47 (s, 1 H), 9.08 (s, 1 H), 7.93 (s, 1 H), 7.82 (s, 1 H), 4.44 (s, 3 H) and 4.40 ppm (s, 3 H); UV (ether) ($\epsilon \times 10^{-3}$) 249 (18), 274 (12), 362 (sh 4.7), and 408 nm (6.7). Anal. Calcd for $C_8H_6N_3O_2Br$: C, 37.50; H, 2.34. Found: C, 37.66; H, 2.50.

Reaction of 5,7-Diiodo-2-methyl-2*H*-cyclopenta[*d*]pyridazine with Silver Nitrite. To a solution of the 5,7-diodo compound[9] prepared from the reaction of 31.9 mg (0.27 mmol) of **1** and 241.9 mg (1.06 mmol) of NIS in 11 mL of CH_2Cl_2 was added 5 mL of Me_2SO and a large excess of $AgNO_2$. The procedure (above) for the reaction with the 5,7-dibromo compound was followed except the reaction time was 4.5 h. The yellow solid (28.1 mg, 38.6% yield from **1**), mp 214–215 °C, was indicated to be a 1:1 mixture of **6** and **7** by its spectra: NMR (trifluoroacetic acid) δ 9.54 (s, 1 H), 8.95 (s, 0.5 H), 8.85 (s, 0.5 H), 8.07 (s, 0.5 H), 7.97 (s, 0.5 H), and 4.62 ppm (s, 3 H); UV (ether) ($\epsilon \times 10^{-3}$) 250 (16), 275 (13), 365 (4), and 410 nm (6.2). Anal. Calcd for $C_8H_6N_3O_2I$: C, 31.68; H. 1.98; N, 13.85. Found: C, 31.83; H, 2.11; N, 13.70.

5,7-Di(acetoxymercuri)-2-methyl-2*H*-cyclopenta[*d*]pyridazine (8). A mixture of 190.2 mg (0.597 mmol) of mercuric acetate and 35.8 mg (0.271 mmol) of **1** in 7 mL of methanol was stored in the dark for 18 h. The dried yellow crystals which formed amounted to 112.6 mg (65%) of **8** after washing with methanol and ether: darkening above 100 °C but no melting up to 265 °C; NMR (Me_2SO) δ 9.14 (s, 1 H), 8.92 (s, 1 H), 7.27 (broad, 1 H), and 4.19 ppm (s, 3 H); UV (THF) (D_{max}) 321 (1.74), 322 (1.80), 389 (0.41), and after dilution 260 nm. Anal. Calcd for $C_{12}H_{12}N_2O_4Hg_2$: C, 22.19; H, 1.89; N, 4.31. Found: C, 22.28; H, 2.15; N, 4.41.

Reaction of 1 with Tetracyanoethene. The addition of a mixture of 296 mg (2.24 mmol) of **1** and 10 mL of benzene to 283 mg (2.21 mmol) of tetracyanoethene in 10 mL of benzene at reflux temperature caused immediate darkening of the solution. After the addition of 3 drops of pyridine and 45 min under reflux, removal of the solvent and chromatography (silica gel column, 1:1 dry ether–ethyl acetate) gave as the first fraction 213 mg (41%) of **9** as maroon crystals, mp 244–248 °C after recrystallization from ethyl acetate and 247–248 °C after two further recrystallizations from acetone: NMR (acetone, CAT) 9.56 (s, 1 H), 9.09 (s, 1H), 8.29 (d, 1 H, J = 4.5 Hz), 7.06 (d, 1 H, J = 4.5 Hz), and 4.59 (s, 3 H); UV (ether)(D_{max}) 496 (0.70), 469 (0.44), 388 (0.09), and 261 nm (0.30); IR ($HCCl_3$) 2203 cm^{-1} (CN). Anal. Calcd for $C_{13}H_7N_5$: C, 66.95; H, 3.02; N, 30.03. Found: C, 66.96; H, 3.28; N, 30.21.

The second fraction was a mixture of **9** and other compounds and, after **9** was absent (TLC), 29.3 mg of red solid was obtained which after rechromatography (ethyl acetate) gave 18.6 mg (4%) of crystals, mp 227–231 °C, partially characterized as **10**: mp 229–230 °C after recrystallization from acetone; NMR (acetone, CAT) δ 9.51 (s, 1 H), 9.37 (s, 1 H), 8.12 (d, 1 H, J = 5 Hz), 7.07 (d, 1 H, J = 5 Hz), and 4.52 (s, 3 H); UV (ether)(D_{max}) 477 (0.26) and 4.54 nm (0.18); IR ($HCCl_3$) 2197 cm^{-1} (CN); mass spectrum m/e 233.076 (calcd for $C_{13}H_7H_5$: 233.070).

Registry No.—**1**, 22291-85-6; **2**, 65275-84-5; **3**, 65275-85-6; **4**, 65275-86-7; **5**, 65275-87-8; **6**, 65275-88-9; **7**, 65275-89-0; **8**, 65275-90-3; **9**, 65275-91-4; **10**, 65275-92-5; $AgNO_2$, 7783-99-5; 7-bromo-2-methyl-2*H*-cyclopenta[*d*]pyridazine, 55268-19-4; tetranitromethane, 509-14-8; 5,7-dibromo-2-methyl-2*H*-cyclopenta[*d*]pyridazine, 55268-20-7; 5,7-diodo-2-methyl-2*H*-cyclopenta[*d*]pyridazine, 55268-23-0; mercuric acetate, 1600-27-7; tetracyanoethene, 670-54-2.

References and Notes

(1) Support from the National Science Foundation (GP-9293 and GP-24623) is gratefully acknowledged.
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2-Aminomethylimidazole and Imidazole-2-carboxaldehyde: Two Facile Syntheses

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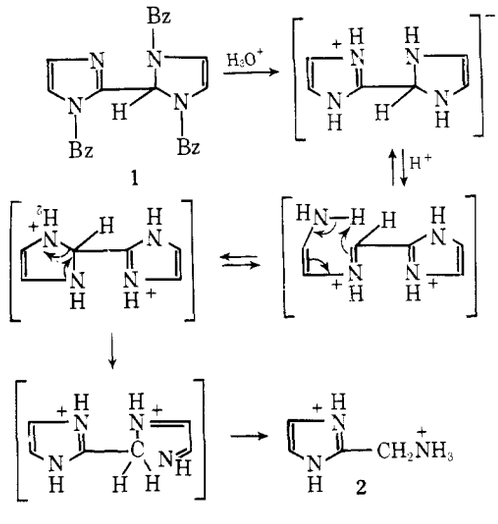
Received September 22, 1977

Interest in our laboratories has been directed toward elaborating methodologies for introducing functionality onto imidazoles available in bulk.[1,2] In a recent publication Regel described the reaction of imidazole with 3 equiv of benzoyl chloride; this led to compound **1**. The functionality latently



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