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A 10-π-Electron Heterocycle: 2,3,4-Tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine

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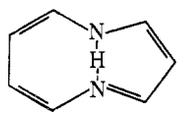
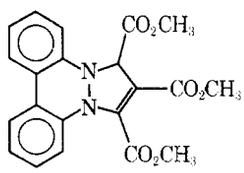
Several years ago we reported[1] the synthesis of some novel heterocycles as potential precursors to derivatives of the 10-π-electron 1,5-diazonine system, **1**, in which the intraannular hydrogen repulsions inhibiting coplanarity in some other potentially aromatic 10-π-electron systems might be relieved by transannular hydrogen bridging as shown.[2]



1

Although we did prepare a number of novel heterocycles, including 1,2,3-tricarbomethoxy-1*H*-benzo[*c*]pyrazolo[1,2-*a*]cinnoline (**2**), we were not able to effect the conversion of any of them to 1,5-diazonine derivatives, as in eq 1, by any conditions then tried. Others have reported both theoretical[4] and experimental[5] studies of some of the heterocycles we discussed, but 1,5-diazonine and its derivatives have not yet appeared in the literature. We now wish to report the successful conversion of **2** to 2,3,4-tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine (**3**, M = H) and some of its derivatives.



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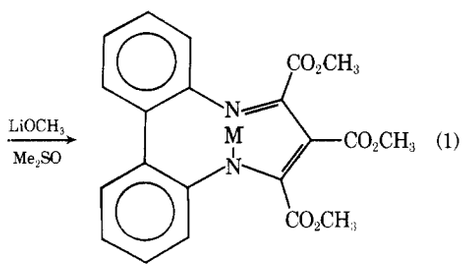
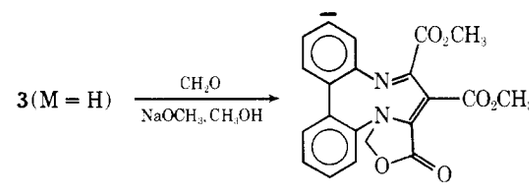


3

When a yellow solution of **2** in dimethyl sulfoxide (Me_2SO) is added to a suspension of 2 equiv of lithium methoxide in Me_2SO, the initially formed intense blue-green color slowly fades to an orange yellow. The bright yellow salt (73%, mp 227–230 °C) obtained on workup could not be purified satisfactorily by recrystallization, but analyzed moderately well for the lithium salt of **3** (**3**, M = Li)[6] containing 0.7 equiv of lithium hydroxide. The use of only 1 equiv of lithium methoxide in the reaction gave less than 50% of the product. Sodium methoxide (2 equiv) worked as well, but potassium methoxide was less effective. Acidification of an aqueous solution of the salt with acetic acid gave the more tractable pale yellow **3**, M = H (80%, mp 110–140 °C). Again, only moderately satisfactory combustion analyses could be obtained on chromatographically purified material; but the 1:1 crystalline solvate with Me_2SO (mp 145–147 °C) gave excellent analytical results. The substance also formed well-defined crystalline solvates with carbon tetrachloride and with acetone.

The structure of **3**, M = H, was established by its spectroscopic properties and some chemical transformations. Thus, the methyl ester functions revealed themselves in the IR (1740, 1710 cm^{-1}) and NMR [δ 3.61 (6 H, s), 3.53 (3 H, s)], as did the proton on nitrogen (3380 cm^{-1}, δ 6.76, washed out with D_2O). Rapid proton exchange at 30 °C between the nitrogens in **3**, M = H, resulting in NMR equivalence of the flanking ester methyls, was suggested by the separation of the lower field, six-hydrogen singlet (δ 3.61) into a broad doublet at −10 °C, whose higher field signal merged with the higher field singlet (δ 3.53) at −30 °C to give two peaks of reversed intensity at δ 3.63 (3 H, s) and 3.55 (6 H, broad singlet). The prototropic change was more clearly revealed in the ^{13}C NMR, which transformed from three peaks for the ester methyl carbons (δ 51.7, 52.7, 53.1) at 25 °C to only two peaks (51.5, 52.6) at 50 °C with an accompanying, though less easily interpretable, simplification of the olefinic–aromatic carbons (δ ~120–170). The higher temperature required for equivalence of the methyl signals in the ^{13}C NMR than in the ^1H NMR presumably reflects the larger chemical shift difference. The substance could be converted with methyl iodide and potassium carbonate to the nicely crystalline, yellow *N*-methyl (NMR δ 2.80) derivative **3**, M = CH_3 (68%, mp 203–205 °C), in which all three ester methyls were now differentiated in the NMR (δ 3.61, 3.66, 3.81). Reaction of **3**, M = H, with formaldehyde and sodium methoxide in methanol gave orange-yellow, crystalline lactone **4** (36%, mp 184–186 °C). The lactone



4

carbonyl was revealed by the IR absorption (1812 cm^{-1}), while the NMR of the two different methylene protons betrayed the conformational rigidity of the system (δ 4.68, 1 H, d, J = 6 Hz, 5.28, 1 H, d, J = 6 Hz[7]). Other spectroscopic data were consistent with structure **4**. Hydrolysis of **3**, M = H, with hot aqueous potassium hydroxide afforded an 85% yield of *o,o'*-diaminobiphenyl, thereby confirming that the N–N bond of **2** had been cleaved, and that more deep-seated transformations of the aromatic nuclei had not taken place. Samples of **3**, M = H, stored for several years in the solid state, showed no evidence of reconversion to any **2**.

The heavy substitution by fused benzene rings and carbo-

methoxy groups in 3 precludes speculation about the presence of bridging or aromaticity in its derivatives. However, the ring opening reaction is novel and may be applicable to less highly substituted derivatives.

Experimental Section

Melting points (uncorrected) were measured on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were taken on a Perkin-Elmer 137 IR spectrophotometer. NMR spectra were recorded on a Varian T-60 (^{1}H NMR) or CFT-20 (^{13}C NMR) and are reported as δ values downfield from Me_4Si (δ 0.0) internal standard. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 instrument. Combustion analyses were performed by Spang Microanalytical Laboratories.

2,3,4-Tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine Lithium Salt (3, M = Li). To a stirred suspension of 285 mg (7.5 mmol) of CH_3OLi in 20 ml of dry Me_2SO in an atmosphere of N_2 was added a solution of 1.477 g)3.75 mmol) of the orange-yellow triester **2** [λ_{max}, (CH_3OH) 260 nm, ϵ ~6300; 295, ~1700; 382, ~2400) in ~10 ml of Me_2SO. A blue-green coloration instantly formed (λ_{max} 588 nm) which on further stirring at room temperature (~90 min) discharged to give an orange-yellow solution (λ_{max} 300 nm, sh 410 nm). The solvent was removed in vacuo (oil bath temperature 80–90 °C), and the viscous brown residue was triturated with chloroform and allowed to stand for 1–2 h. The bright yellow salt was filtered and washed with $CHCl_3$ until the filtrate was colorless. The vacuum dried salt weighed 1.1 g (73%) and had mp 227–230 °C dec. (Use of only 1 equiv of CH_3OLi yields only 50% Li salt.) Attempts to crystallize the product were not successful. NMR (Me_2SO-d_6) δ 6.35–7.30 (8 H, m), 3.47 (6 H, s), 3.22 (3 H, s), no other absorption observed from −4 to 15; IR (Nujol) 1754, 1740, 1660 cm^{-1}; UV (Me_2SO) λ_{max} 310 nm (ϵ ~12 800), 410 (~2800). An analytical sample was washed well with $CHCl_3$ and dried at 60 °C in vacuo.

Anal. Calcd for $C_{21}H_{17}N_2O_6Li$: C, 63.00; H, 4.28; N, 6.99; Li, 1.73. Calcd for $C_{21}H_{18}N_2O_7Li_2$: C, 59.46; H, 4.28; N, 6.60; Li, 3.27. Calcd for $C_{21}H_{17}N_2O_6Li$ (0.7 LiOH): C, 60.47; H, 4.28; N, 6.72; Li, 2.83. Found: C, 60.56; H, 4.25; N, 6.98; Li, 2.83.

2,3,4-Tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine (3, M = H). Li salt 3 (M = Li) (1.0 g) was dissolved in 30 ml of H_2O and filtered. The clear yellow filtrate was acidified with 50% acetic acid to pH 7. The pale-yellow solid which separated was filtered, washed with H_2O, and dried in vacuo over $CaCl_2$ to give 0.76 g (~80%): mp 110–140 °C; NMR ($CDCl_3$) (33 °C) δ 6.5–7.5 (9 H, m), 3.61 (6 H, s), 3.53 (3 H, s); (10 °C) 3.58, 3.62 (br, 6 H), 3.54 (3 H, s); (−30 °C) 3.62 (3 H, s), 3.55 (6 H, br, s); ^{13}C NMR ($CDCl_3$) (50 °C) 51.5, 52.6, 127–166 (six broad peaks); (25 °C) 51.7, 52.7, 53.1, 124–166 (16 peaks). Addition of a few drops of D_2O to an acetone complex of the amino ester in $CDCl_3$ washed out a resonance at 6.75. NMR (Me_2SO-d_6) δ 9.2 (broad, s), 6.5–7.5 (m), 3.6 (s) 3.48 (s). Addition of D_2O washed out the absorption at 9.2. IR (Nujol) 3320 (broad), 1740, 1695, 1640 cm^{-1}. IR ($CHCl_3$) 3380 (sharp), 1740, 1710, 1650 cm^{-1}.

An analytical sample was prepared by chromatographing 600 mg of the product over 100 g of Merck Al_2O_3, eluting with $CHCl_3$–C_6H_6 (1:3), and collecting the yellow band. TLC of this material gave a single spot. The product was freed from solvent by heating to 150 °C in vacuo for 3 h to give material of mp 110–140 °C. TLC of the dried sample showed only one component.

Anal. Calcd for $C_{21}H_{18}N_2O_6$: C, 63.95; H, 4.60; N, 7.10. Found: C, 64.74, H, 4.91; N, 6.80.

Samples stored for several years showed unchanged NMR spectra.

Formation of Solvates. The amino ester forms solvates with almost all solvents tried (CCl_4, acetone, dimethyl sulfoxide). Recrystallization from CCl_4 gives a product which begins to froth at 100 °C. A weighed amount of this sample when heated to 130–140 °C in vacuo showed a loss in weight of 1418%. The IR spectrum remained unchanged.

A concentrated solution of the material in acetone gradually deposits a nicely crystalline product, mp 120 °C (frothing). An NMR ($CDCl_3$) of this sample shows the acetone singlet (δ 2.0).

Particularly stable is the Me_2SO complex. The amino ester (450 mg) was shaken well with 3.5 ml of dry Me_2SO and filtered from a small amount of insoluble material, and the clear filtrate was treated dropwise with H_2O until a cloudiness persisted. After 2 h at room temperature, the crystalline material was filtered, washed with water, and dried over $CaCl_2$ in vacuo to give 348 mg (~75% recovery), mp 145–147 °C. A sample for analysis was dried at 90–95 °C in vacuo for 2 h: NMR ($CDCl_3$) δ 6.5–7.5 (m), 3.62 (6 H, s), 3.56 (3 H, s), 2.5 (6 H, s); IR (Nujol) 3180 (w), 3270 (w), 1745, 1730, 1710, 1650 cm^{-1}. Heating a sample at 150–155 °C in vacuo for 20 min resulted in removal of only ~30% Me_2SO as indicated by NMR.

Anal. Calcd for $C_{21}H_{18}N_2O_6$·C_2H_6SO: C, 58.46; H, 5.12; N, 5.93. Found: C, 58.54; H, 5.12; N, 5.84.

***N*-Methyl-2,3,4-tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine (3, M = CH_3).** Ester 3, M = H (197 mg, 0.5 mmol), CH_3I (0.9 mmol), and K_2CO_3 (0.6 mmol) were stirred in 10 ml of methanol at room temperature overnight. CH_3OH was removed in vacuo, and the residue was dissolved in benzene and filtered. Pentane was added dropwise to a concentrated benzene solution until crystals begin to separate. After a few hours, the crystalline material was filtered and dried in vacuo to give 140 mg of yellow crystals (68%): mp 203–205 °C; NMR ($CDCl_3$) δ 6.75–7.60 (8 H, m), 3.81 (3 H, s), 3.66 (3 H, s), 3.61 (3 H, s), 2.8 (3 H, s); mass spectrum parent peak *m/e* 408.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.71; H, 4.94; N, 6.86. Found: C, 64.91; H, 4.87; N, 6.74.

Hydrolysis of Amino Ester 3, M = H. Amino ester 3, M = H (245 mg, 0.62 mmol) was dissolved in 20 ml of hot 4 N KOH and refluxed in an oil bath. After 5 h the mixture was allowed to cool, whereby the oily droplets which had formed solidified. These were filtered and washed with water. The filtrate was heated to 100 °C for another 5 h, then allowed to stand at room temperature overnight. The insoluble material was again filtered. Heating the filtrate for another 8 h and allowing to cool yielded another 10 mg of product. The total yield of *o,o'*-diaminobiphenyl was 94 mg (85%). Recrystallization from cyclohexane gave shiny plates: mp 78–80 °C (lit. mp 80 °C); NMR ($CDCl_3$) δ 6.5–7.2 (8 H, m), 3.6 (4 H, broad m); IR ($CHCl_3$) 3497, 3401, 3030 cm^{-1}; mass spectrum parent peak *m/e* 184.

Reaction of 3, M = H, with Formaldehyde. Formation of Lactone 4. Amino ester 3, M = H (556 mg, 1.41 mmol), CH_3ONa (15 mg, 0.3 mmol), and a solution of formaldehyde in dry methanol (6 ml, 0.1 g/ml) were stirred at room temperature overnight. The solvent was removed in vacuo and the residue extracted with 40 ml of hot benzene–cyclohexane (60:40 my volume). The filtrate was allowed to stand for 3 h, the insoluble material filtered, and the filtrate concentrated to 25 ml. The insoluble material which separated was again filtered. The filtrate was finally concentrated to 10 ml and allowed to crystallize overnight. The orange-yellow crystals were filtered to give 150 mg, mp 178–180 °C. Further concentration of filtrate yielded another 50 mg of product, mp 180–182 °C, to give a total yield of 200 mg (36%). An analytical sample, mp 184–186 °C, was obtained by recrystallization from a 60:40 mixture of benzene–cyclohexane: mass spectrum parent peak *m/e* 392; IR (Nujol) 1812, 1761, 1709, 1653 cm^{-1}; NMR ($CDCl_3$) δ 6.7–7.6 (8 H, m), 5.28 (1 H, d, J = 6 Hz), 4.68 (1 H, d, J = 6 Hz), 3.75 (3 H, s), 3.73 (3 H, s).

Anal. Calcd for $C_{21}H_{16}N_2O_6$: C, 64.28; H, 4.11; N, 7.14. Found: C, 64.42; H, 4.15; N, 7.14.

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Registry No.—**2**, 7593-55-7; **3** (M = Li), 60734-18-1; **3** (M = H), 60734-19-2; **3** (M = CH_3), 60734-20-5; **4**, 60734-21-6; *o,o'*-diaminobiphenyl, 1454-80-4; formaldehyde, 50-00-0.

References and Notes

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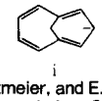
(2) A completely planar 1 would require either an abnormally short N–H· · ·N distance (ca. 1.6 Å) or an abnormally open C–N=C bond angle (ca. 180°). However, distortion from coplanarity with the resulting bent N–H· · ·N bond could relieve these strains considerably without complete loss of delocalization as illustrated by the anion i.[3]



i

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(6) Structures of derivatives of **3** are drawn with the trans C=N as though bridged only from convenience and prejudice. We have little information on the configurations or conformations of these compounds, although it is clear that **3**, M = H, does not exist in a symmetrically hydrogen-bonded form (vide infra).

(7) The small geminal coupling constant probably reflects increased s character from the electronegative substituents and strained ring.