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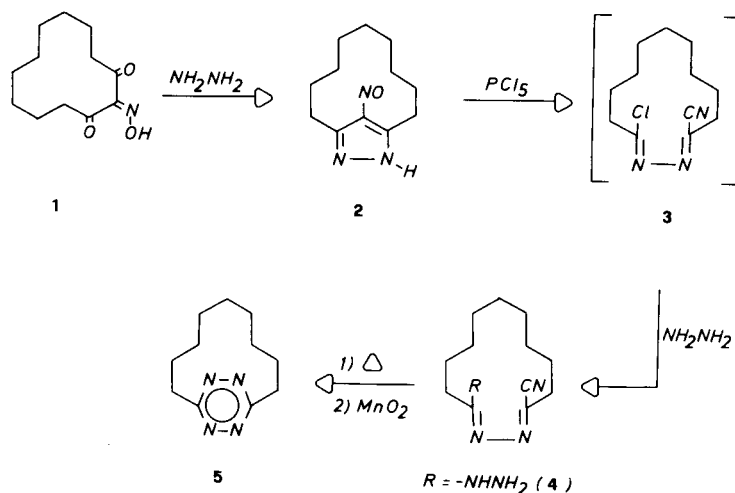
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The first synthesis of a tetrazinophane, from 2-nitrosocyclododecane-1,3-dione, is reported.

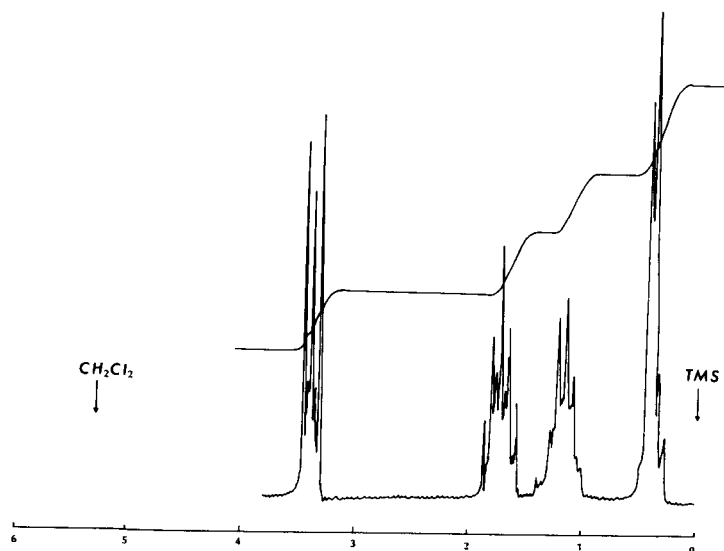
J. Heterocyclic Chem., **18**, 685 (1981).

As part of our studies in the heterophanes field (1) we now report the synthesis of the [9][3,6]-s-tetrazinophane (5). The synthesis has been accomplished starting from 2-nitrosocyclododecane-1,3-dione (1) and it is based on the well known chemical behaviour of 4-nitrosopyrazoles (2), according to the following scheme.

2-Nitrosocyclododecane-1,3-dione (1) was obtained from cyclododecane-1,3-dione (3) on treatment with sodium nitrite in acetic acid. 4-Nitroso[9][3,5]pyrazolophane (2) was prepared from 1 by reaction with hydrazine hydrate in boiling methanol (4). Phosphorus pentachloride reacts briskly with 2 giving 3-cyano-13-chloro-1,2-diazacyclotri-



Scheme 1



NMR [90 MHz, deuteriochloroform, room temperature] of 5.

deca-13(1),2(3)-diene (**3**). Compound **3** is an undistillable oil which is very sensitive to moisture; it was used without any characterization (**5**). 3-Cyano-13-hydrazino-1,2-diazacyclo-trideca-13(1),2(3)-diene (**4**) was obtained from **3** by reaction with hydrazine hydrate.

The title compound (**5**) was prepared from the hydrazinocyno derivative (**4**) by thermal cyclization and active manganese dioxide oxidation. The nmr spectrum of **5** is shown in Figure 1.

The absorptions due to the nonamethylene protons of **5** were composed of four groups of multiplets (intensity: 4:4:4:6). Unlike the [9][2,5]pyridinophane (**6**), the tetrazine ring in **5** can rotate along its axis relative to the nonamethylene chain (indeed the absorption at δ 3.32, due to the benzylic protons, can be approximately regarded as a triplet). This fact may be ascribed to the increase in the aza substitution that causes a contraction of the aromatic ring (**7**).

The comparison of the uv spectrum of **5** with that of 3,6-dialkyl-s-tetrazines (**8**) shows a hypsochromic shift (of about 27 nm) of the $n\pi^*$ absorption as the only difference. At the moment we cannot make any comment on this fact. The nmr spectrum of **5** remained unchanged up to ca. -130°.

EXPERIMENTAL

Melting points were taken on a Buchi apparatus and are uncorrected. ¹H Nmr spectra were obtained on a Varian EM 390 instrument, chemical shifts are reported in δ from internal TMS and refer to the center of the signal. Infrared spectra were recorded on a Perkin-Elmer 377 spectrophotometer. Uv spectra were taken on a Varian Cary 219 (ethanol solutions). Mass spectra were obtained with a Varian MAT 311-A mass spectrometer equipped with a combined FI, FD and EI ion source. Column chromatography were performed on Merck Kieselgel 60, 0.063-0.200 mm. Magnesium sulphate was used as drying agent. Evaporation was carried out *in vacuo* (rotary evaporator).

2-Nitrosocyclododecane-1,3-dione (**1**).

Cyclododecane-1,3-dione (**3**) (8 g.) was dissolved in acetic acid (55 ml.) and water (5 ml.) and then a solution of sodium nitrite (8 g.) in water (20 ml.) was added dropwise with stirring at 5°. After 10 minutes the solution was poured into water (200 ml.) and extracted with dichloromethane (3 x 100 ml.). The extracts were washed with water and dried. Solvent evaporation afforded the 2-nitroso cyclododecane-1,3-dione (**1**) (7.8 g., 85%), m.p. 81-82° from ether-pentane; nmr (deuteriochloroform): 10.1 (1H, s), 2.7 (4H, m), 1.9-1.2 (14H, m); ir (nujol): 3225, 3175, 1690, 1000 cm^{-1} ; uv: λ max 237 nm (9,690); m/z 225 (M^+) (4), 41 (100).

Anal. Calcd. for $\text{C}_{12}\text{H}_{19}\text{NO}_3$: C, 63.97; H, 8.50; N, 6.22. Found: C, 64.10; H, 8.59; N, 6.15.

4-Nitroso[9][3,5]pyrazolophane (**2**).

A solution of 2-nitrosocyclododecane-1,3-dione (**1**) (9 g.) in methanol (140 ml.) was heated under reflux and then hydrazine hydrate (1.7 g.) in methanol (40 ml.) was added dropwise with stirring (30 minutes) (**4**). After 1 hour, the solution was evaporated, water was added (150 ml.) and the mixture was extracted with dichloromethane (3 x 100 ml.). The extracts were washed with 9% hydrochloric acid, water and dried. Solvent

evaporation afforded 4-nitroso[9][3,5]pyrazolophane (**2**) (7.1 g., 80%), m.p. 131-132° from ether-pentane; nmr (deuteriochloroform): 13.1 (1H, s), 3.38 (2H, m), 2.71 (2H, m), 1.6-0.83 (12H, m), 0.31 (2H, m), ir (nujol): 3180, 3100, 1580 cm^{-1} ; uv: λ max 304 nm (10,100), 675 nm (65); ms: m/z 221 (M^+) (11), 41 (100).

Anal. Calcd. for $\text{C}_{12}\text{H}_{19}\text{N}_3\text{O}$: C, 65.12; H, 8.65; N, 18.99. Found: C, 64.91; H, 8.52; N, 19.12.

3-Cyano-13-hydrazino-1,2-diazacyclo-trideca-13(1),2(3)-diene (**4**).

4-Nitroso[9][3,5]pyrazolophane (**2**) (7 g.) was dissolved in dichloromethane (100 ml.) and the solution was cooled at 0°. Phosphorus pentachloride (9 g.) was then added slowly, with stirring. After 10 minutes at room temperature, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluant dichloromethane) giving 3-cyano-13-chloro-1,2-diazacyclo-trideca-13(1),2(3)-diene (**3**) (**5**) (6 g., 78%). To a solution of **3** (6 g.) in acetonitrile (100 ml.), hydrazine hydrate (5 g.) was added. The mixture was stirred for 30 minutes at room temperature, water (100 ml.) was added, and the solution was cooled at 0°. Filtration afforded the 3-cyano-13-hydrazino-1,2-diazacyclo-trideca-13(1),2(3)-diene (**4**) (4.6 g., 78%), m.p. 144-145° from dichloromethane-pentane; nmr (deuteriochloroform): 7.3 (1H, s), 3.8 (2H, m), 2.8 (2H, m), 1.9-1.2 (14H, m); ir (nujol): 3340, 3300, 3200, 2220, 1640 cm^{-1} ; uv: λ max 295 nm (9,550); ms: m/z 235 (M^+) (4), 41 (100).

Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{N}_5$: C, 61.24; H, 9.00; N, 29.76. Found: C, 61.45; H, 9.00; N, 29.50.

[9][3,6]-s-Tetrazinophane (**5**).

3-Cyano-13-hydrazino-1,2-diazacyclo-trideca-13(1),2(3)-diene (**4**) (1 g.) was heated, under nitrogen, at 180° for 15 minutes. After cooling, dichloromethane (50 ml.) and then active manganese dioxide (2 g.) were added. After 10 minutes of stirring the mixture was filtered, the solvent evaporated and the residue purified by silica gel (15 g.) column chromatography (eluant pentane-ether 20:1 v:v) giving the [9][3,6]-s-tetrazinophane (**5**) (0.34 g., 39%), b.p. 115-120° at 0.25 mm; nmr (deuteriochloroform): 3.32 (4H, m), 1.66 (4H, m), 1.1 (4H, m), 0.38 (6H, m); ir (film): 1640 cm^{-1} ; λ max 265 nm (2,300), 280 nm (2,500), 513 nm (410); ms: m/z 206 (M^+) (2), 41 (100).

Anal. Calcd. for $\text{C}_{11}\text{H}_{18}\text{N}_4$: C, 64.04; H, 8.80; N, 27.16. Found: C, 64.23; H, 8.87; N, 26.92.

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- 4) A quick addition of hydrazine hydrate gave in part reduction of the nitroso group with formation of the 4-amino[9][3,5]pyrazolophane, m.p. 130-132° from ether-pentane; nmr (deuteriochloroform): 4.9 (3H, bs), 2.6 (4H, m), 1.7-0.9 (13H, m), 0.48 (2H, m); ir (nujol): 3100-3400, 1620 cm^{-1} ; uv: λ max 247 (3,800); ms: m/z 207 (M^+) (78), 42 (100).
Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{N}_3$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.23; H, 10.11; N, 20.12.
- 5) In the presence of moisture, **3** slowly afforded a product to which the structure of 3-cyano-13-oxo-1,2-diazacyclo-trideca-2(3)-ene was assigned on the basis of analytical and spectroscopic data, m.p. 87-88° from hexane; nmr (deuteriochloroform): 9.1 (1H, s), 2.6 (4H, m), 1.8-1.3 (14H, m); ir (nujol): 3400, 3200, 3120, 2230, 1700, 1605 cm^{-1} ; uv: λ max 233 (7,500), 268 (11,000); ms: m/z 221 (M^+) (4), 41 (100) (Anal. Calcd. for $\text{C}_{12}\text{H}_{19}\text{N}_3\text{O}$: C, 65.12; H, 8.65; N, 18.99. Found: C, 64.96; H, 8.69; N, 18.71).
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