bridgehead H(5)), 2.36 (dd of m (half), 1 H, *J* = 18, *J* = 7.5, *J* = 1.8 Hz, H(6)), 2.50 (s, 3 H, CH_3 (Ts)), 1.84 (d of m, 1 H, *J* = 18 Hz, H(6)); ^{13}C NMR δ 77.7 d (C(1)), 71.3 s (C(4)), 57.0 d (C(5)), 35.5 t (C(6)), 21.7 q (CH_3); mass spectrum *m/e* 476 (24, M^+), 321 (100, M^+ – Ts), 288 (5, M^+ – Ts – HS), 255 (9, M^+ – Ts – cyclopentadiene).

Anal. Calcd for $C_{25}H_{20}N_2O_4S_2$: C, 63.02; H, 4.23; N, 5.88; S, 13.44. Found: C, 62.91; H, 4.26; N, 5.81; S, 13.29.

21: mp 207–208 °C; IR (KBr disk) 1520, 1340 ($\nu(NO_2)$), 1160, 1090 ($\nu(SO_2)$); ^1H NMR δ 8.8–7.3 (m, 11 H, aromatic), 5.90 (s of m, 2 H, olefinic H(7,8)), 5.59 (d of m, 1 H, *J* = 7.5, *J* = 2.4, *J* = 1.2 Hz, bridgehead H(1)), 3.69 (dt, 1 H, *J* = 7.5, *J* = 7.5, *J* = 2.0 Hz, bridgehead H(5)), 2.49 (s, 3 H, CH_3 (Ts)), 2.36 (dd of m (half), 1 H, *J* = 18, *J* = 7.5, H(6)), 1.98 (d of m, 1 H, *J* = 18 Hz, H(6); ^{13}C NMR δ 77.9 d (C(1)), 71.2 s (C(4)), 56.1 d (C(5)), 35.6 t (C(6)), 21.6 q (CH_3); mass spectrum *m/e* 476 (24, M^+), 321 (100, M^+ – Ts), 288 (5, M^+ – Ts – HS), 255 (9, M^+ – Ts – cyclopentadiene).

Anal. Calcd for $C_{25}H_{20}N_2O_4S_2$: C, 63.02; H, 4.23; N, 5.88; S, 13.44. Found: C, 63.05; H, 4.25; N, 5.90; S, 13.32.

Registry No. 1a, 63609-88-1; **1b**, 63609-89-2; **2a**, 109-92-2; **2b**, 111-34-2; **2c**, 109-53-5; **3a**, 68380-36-9; **3b**, 68380-37-0; **3c**, 68380-38-1; **3d**, 70179-31-6; **5**, 2403-57-8; **6**, 70179-32-7; **7a**, 670-80-4; **7b**, 2981-10-4; **8a**, 70179-33-8; **8b**, 70179-34-9; **9a**, 70179-35-0; **9b**, 70179-36-1; **10**, 121-46-0; **11**, 70208-93-4; **12**, 498-66-8; **13**, 70179-37-2; **14a**, 513-81-5; **14b**, 78-79-5; **14c**, 504-60-9; **15a**, 70179-38-3; **15b**, 70179-39-4; **15c**, 70179-40-7; **16b**, 68380-34-7; **16c**, 68380-35-8; 18, 542-92-7; **19**, 70179-41-8; **20**, 70179-42-9; **21**, 70223-54-0.

Novel Rearrangement of a [2.2](2,5)Pyrrolophane

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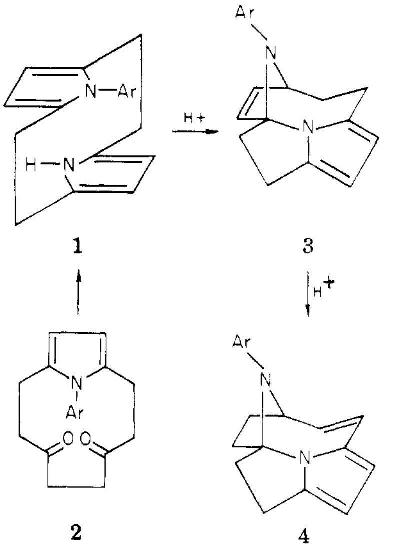
N-(*p*-Bromophenyl)[2.2](2,5)pyrrolophane (1), when treated with acid, forms, successively, 13-(*p*-bromophenyl)-13,14-diazatetracyclo[8.2.1.$1^{4,7}$.$0^{1,14}$]tetradeca-4,6,11-triene and its 2,6,11-triene isomer (4). A possible mechanism, involving an aziridinium ion intermediate, is suggested.

Scheme I



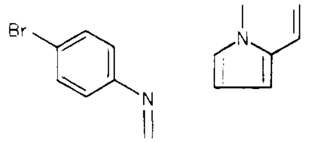
Ar = C_6H_4Br

Table I. Crystal Data

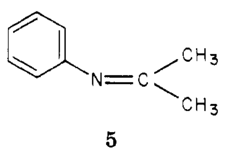
compd	$C_{18}N_2H_{17}Br$
mol wt	341.3
μ	28.61 cm^{-1}
ρ(obsd)	1.50 (2) g cm^{-3}
ρ(calcd)	1.49 g cm^{-3}
max crystal dimensions	0.30 × 0.45 × 0.50 mm
space group	$P2_1$
Z	2
cell constants	
a = 6.991 (5) Å	
b = 10.497 (6) Å	
c = 10.452 (6) Å	
β = 98.10 (4)°	
V	759.43 $Å^3$

We have recently described[1] the synthesis of *N*-(*p*-bromophenyl)[2.2](2,5)pyrrolophane (**1**) from *N*-(*p*-bromophenyl)-3,6-dioxo-[8](2,5)pyrrolophane (**2**) and ammonium acetate (Scheme I). Compound **1** was formed, along with an isomeric material, identified as 13-(*p*-bromophenyl)-13,14-diazatetracyclo[8.2.1.$1^{4,7}$.$0^{1,14}$]tetradeca-4,6,11-triene (**3**), and could also be obtained from compound **2** by treatment with ammonium acetate in dilute aqueous acid.

In some instances, this reaction afforded traces of an additional isomer (**4**) which is isomeric with compounds **1** and **3**. We have now found that a solution of compound **3** in acetic acid, when heated, or in trifluoroacetic acid at room temperature affords this "trace" material in essentially quantitative yield. The ^1H NMR spectrum of this compound is very similar to that of compound **3** except for minor chemical shift changes (cf. Table I). On the other hand, its ultraviolet spectrum [λ_{max} 253, 292, 301 (sh) nm] is significantly different from that of compound **3** (λ_{max} 262 nm). The surprising appearance of these new long-wavelength absorptions in compound **4** can reasonably be explained by the presence of a highly conjugated chromophore. Since compound **3** has two aromatic rings within its structure (phenyl and pyrrole), one might suggest that a double-bond migration into conjugation with either one of these rings has occurred. This would give rise to either one of the partial structures



Since the ultraviolet spectrum of the Schiff base **5**[3] is significantly different from that of compound **4**, the conjugated pyrrole partial structure is a much more at-



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(1) R. L. Mahaffey, J. L. Atwood, M. B. Humphrey, and W. W. Paudler, *J. Org. Chem.*, **41**, 2963 (1976).

(2) J. L. Atwood, W. E. Hunter, H. Alt, and M. D. Rausch, *J. Am. Chem. Soc.*, **98**, 2454 (1976).

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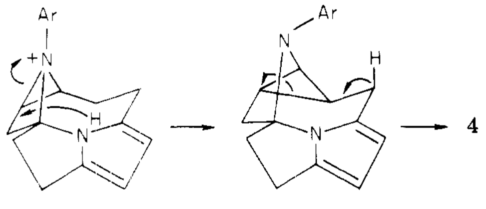
tractive structural candidate. In fact, an X-ray crystallographic structure determination (see supplementary material Table II and Figure 1) confirmed this deduction and established structure 4 as the correct one for this compound (cf. Table II). The number of modes of formation of this isomer from compound 3 is limited by Bredt's rule. Thus, the simple process of two successive 1,3-hydrogen shifts in compound 3 which leads directly to structure 4 must be eliminated. On the other hand, protonation of the double bond aided by participation of the phenyl-substituted nitrogen gives rise to the aziridinium ion 6. This might well be the intermediate leading to compound 4.



6   7

Experimental Section

13-(*p*-Bromophenyl)-13,14-diazatetracyclo[8.2.1.1^{4,7}.0^{1,14}]tetradeca-2,4,6-triene (4). Compound 1[1] (200 mg, 0.86 mmol) was dissolved in 20 mL of glacial HOAc and heated at 100 °C under a nitrogen atmosphere for 1.5 h. The mixture was cooled and poured into a cold, concentrated NH_4OH solution. The product was extracted with $CHCl_3$ (3 × 25 mL), and the extracts were dried over anhydrous K_2CO_3. Chromatography of the crude product on Brockmann grade II silica gel, using 1:1 benzene–cyclohexane as eluent, gave 30 mg of a yellow oil which gradually solidified. Further elution with CH_2Cl_2 gave a trace of *p*-bromoaniline identified by its R_f value from thin-layer chromatography and its mass spectrum. The product was further purified by sublimation (120 °C (0.1 mm)) to give a yellow solid: 160 mg (80%); mp 142–143.5 °C; mass spectrometric mol wt 340 and 342; ^{1}H NMR δ 1.8–3.2 (m, 8 H), 4.70 (br t, 1 H), 5.47 (dd, 1 H), 5.79 (d, 1 H), 6.0–6.4 (m, 4 H), 7.11 (d, 2 H); UV (isooctane), λ_{max} (log ϵ) 253 (3.86), 292 (3.85), 301 (sh) (3.78). Anal. Calcd for $C_{18}H_{17}N_2Br$: C, 63.36; H, 5.03; N, 8.21. Found: C, 63.25; H, 5.03; N, 8.14.

X-ray Data Collection, Structure Solution, and Refinement. A single crystal of 4 was sealed in a thin-walled glass capillary and placed on an Enraf-Nonius CAD-4 diffractometer. Final lattice parameters as determined from a least-squares refinement of the angular settings of 12 accurately centered reflections ($2\theta > 30°$) are given in Table I.

Data were taken on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the θ–2θ scan technique. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. One independent quadrant of data was collected to $2\theta \leq 40°$. This produced 888 independent observed reflections ($I > 3\sigma(I)$). A complete account of the data collection procedure and diffractometer parameters has been given previously.[2]

The existence of two molecules per unit cell in the space group $P2_1$ imposed no crystallographic symmetry.[3] The position of the bromine atom was deduced from a Patterson map, and a subsequent difference Fourier map calculation revealed the positions of all remaining nonhydrogen atoms. In the final cycles of refinement the bromine atom was treated with anisotropic thermal parameters, while the nitrogen and carbon atoms were dealt with isotropically. Hydrogen atoms were placed in calculated positions and unobserved reflections were not used. The final R values were

$$R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.060$$

$$R_2 = \{\sum(|F_o| - |F_c|)^2/\sum F_o^2\}^{1/2} = 0.062$$

The largest parameter shifts in the final cycle were less than 0.10 of their esd's, and a difference Fourier map showed no unaccounted electron density. The final values of the positional and thermal parameters are given in supplementary material Table II.

Registry No. 1, 59547-40-9; 4, 70288-27-6.

Supplementary Material Available: Figure 1 with numbering and Tables II and III containing atomic coordinates and bond lengths and angles (3 pages). Ordering information is given on any current masthead page.

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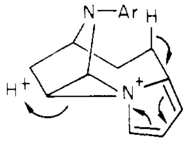
(3) Systematic absences allowed the space group to be either $P2_1/m$ or $P2_1$. Solution and refinement of the structure showed that the latter is the correct choice.

(4) A referee suggested the possible intermediacy of structure 8 followed by the rearrangements shown. An examination of molecular models indicates this to be a rather highly strained structure, in comparison to our proposed structure 7 which requires no significant introduction of strain.



8

Synthetic Routes to Aminodinitrotoluenes

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Synthetic routes to the aminodinitrotoluenes have been investigated and several useful new methods developed. A procedure for selective hydrolysis of polynitro *N*-acyltoluidines permits facile separation of the nitration isomer mixtures. Products formed by reaction of ammonia with isomeric trinitrotoluenes, as well as those from reduction of 2,4,6-trinitrotoluene with hydrogen sulfide, have been separated and identified.

Aminodinitrotoluenes have been identified in our work as major components of waste waters resulting from the manufacture of 2,4,6-trinitrotoluene (α-TNT). They are also formed by ammonolysis and reduction of TNT isomers. In order that their toxicological and explosive properties could be evaluated, convenient synthetic routes to these substances were required. This report describes some new syntheses of aminodinitrotoluenes and im-

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