Fused *s*-Triazino Heterocycles. XVII. 8,13-Dihydro-1,3,7,8,13c-pentaazabenzo[*de*]naphthacene, 7*H*-1,3,7,8,11b,12,14-Heptaazadibenzo[*de*,*hi*]naphthacene and 8*H*-1,3,7,8,13,14c-Hexaazabenzo[4,5]cyclohepta[1,2-*a*]phenalene, Three New Ring Systems

John T. Shaw*, Wendy L. Corbett, Gregory D. Cuny,
Mallory F. Egler and Victoria S. Peciulis

Department of Chemistry, Grove City College,
Grove City, PA 16127

Received January 15, 1991

The reaction of 7,9-dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1a**) with *p*-toluidine is shown to give 4,6-dibromo-2-*t*-butyl-8,13-dihydro-13-imino-11-methyl-1,3,7,8,13c-pentaazabenzo[*de*]naphthacene (**4**) in two steps with 7,9 dibromo-2-*t*-butyl-4-cyano-5-*p*-toluidino-1,3,6,9b-tetraazaphenalene (**2b**) as the intermediate product. A related annulation reaction of **1a** with *N*-(5-amino-2,4-dimethylphenyl)trimethylacetamide (**8**) leads in two steps to 9,11-dibromo-2,13-di-*t*-butyl-4,6-dimethyl-7*H*-1,3,7,8,11b,12,14-heptaazadibenzo[*de*,*hi*]naphthacene (**6**) with 7,9-dibromo-2-*t*-butyl-4-cyano-5*N*-(2,4-dimethyl-5-trimethylacetamidophenyl)amino-1,3,6,9b-tetraazaphenalene (**2d**) as the intermediate product. In a similar fashion the reaction of **1a** with *o*-phenylenediamine forms 14-amino-4,6-dibromo-2-*t*-butyl-8*H*-1,3,7,8,13,14c-hexaazobenzo[4,5]cyclohepta[1,2-*a*]-phenalene (**12**) by way of the intermediate 5-*N*-(2-aminophenyl)amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2e**). The preparation of *N*-(2,4-dimethyl-5-nitrophenyl)trimethylacetamide (**11**) and its reduction to *N*-(5-amino-2,4-dimethylphenyl)trimethylacetamide (**8**) is also described.

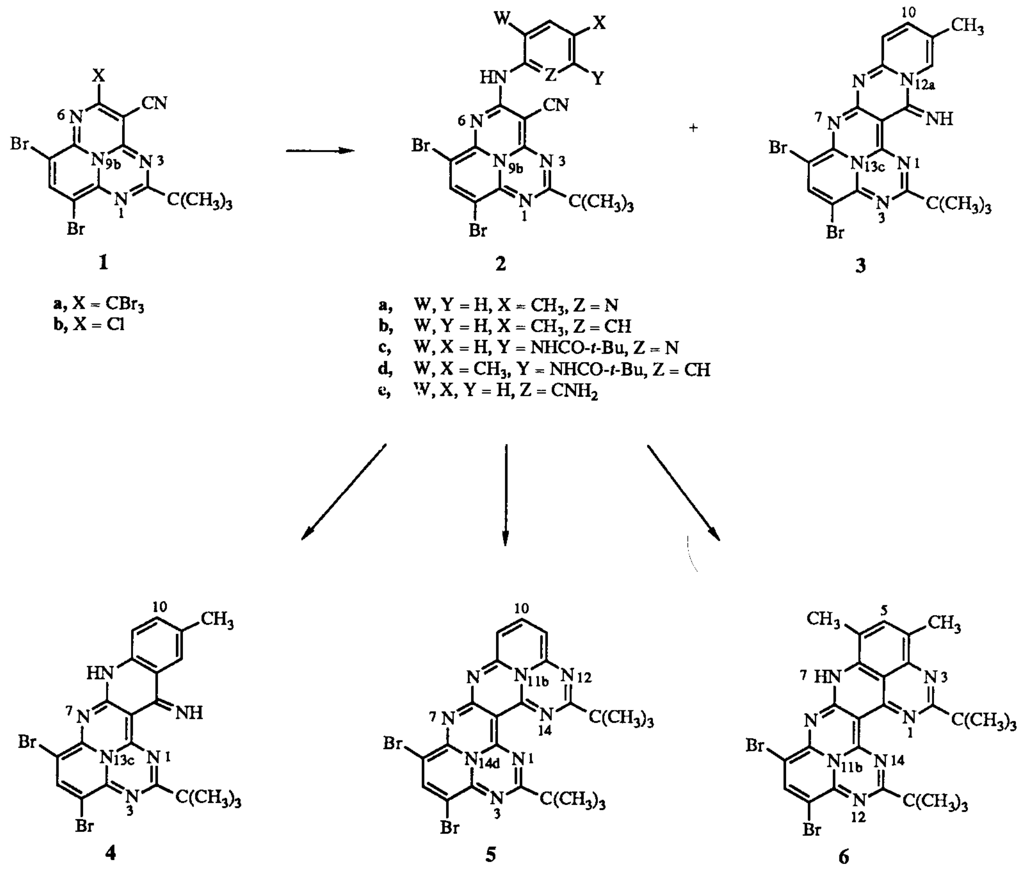
J. Heterocyclic Chem., **28**, 987 (1991).

The preparation of 4,6-dibromo-2-*t*-butyl-13-imino-11-methyl-13*H*-1,3,7,8,12a,13c-hexaazabenzo[*de*]naphthacene (**3**), a member of a new ring system described in a recent paper [1], involved the 4-dimethylaminopyridine (DMAP) catalyzed reaction of 7,9-dibromo-5-tribromomethyl-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**1a**) with 2-amino-5-picoline (**7**). The isomeric product, 7,9-dibromo-2-*t*-butyl-4-cyano-5*N*-(5-methyl-2-pyridyl)amino-1,3,6,9b-tetrazaphenalene (**2a**) also formed at the same time. It was of interest to determine whether an aniline derivative could be substituted for the pyridine moiety in this ring closure. Subsequent experiments showed that the DMAP catalyzed reaction of *p*-toluidine with **1a** in refluxing chloroform would give 7,9-dibromo-2-*t*-butyl-4-cyano-5-*p*-toluidino-1,3,6,9b-tetraazaphenalene (**2b**) in 71% yield. That 4,6-dibromo-2-*t*-butyl-8,13-dihydro-13-imino-11-methyl-1,3,7,8,13c-pentaazabenzo[*de*]naphthacene (**4**) did not form at the same time was not surprising as the phenyl carbon would not be expected to be as nucleophilic as the pyridine nitrogen in **2a**. Ring closure of **2b** to **4** in 85% yield was effected by refluxing **2b** with excess aluminum chloride in chlorobenzene for 1 hour. The structure of **4** was supported by satisfactory elemental analysis, by the presence of NH-absorption and the absence of CN-absorption in the ir and appropriate pmr signals.

With the reaction conditions necessary to bring about the ring closure of **2b** in hand, we wondered about the more interesting possibility of a double ring closure similar to that described in the same paper referred to above [1]. In that case heating 7,9-dibromo-2-*t*-butyl-4-cyano-5-*N*-(6-trimethylacetamido-2-pyridyl)amino-1,3,6,9b-tetraazaphenalene (**2c**) with *p*-toluenesulfonic acid in chlorobenzene for 1 hour gave 4,6-dibromo-2,13-di-*t*-butyl-1,3,7,8,11b,12,14,14d-octaazadibenzo[*de*,*hi*]naphthacene (**5**). Experimentation revealed that refluxing 7,9-dibromo-2-*t*-butyl-4-cyano-5*N*-(2,4-dimethyl-5-trimethylacetamidophenyl)amino-1,3,6,9b-tetraazaphenalene (**2d**) with excess aluminum chloride in chlorobenzene for about 1 hour would give, analogously, 9,11-dibromo-2,13-di-*t*-butyl-4,6-dimethyl-7*H*-1,3,7,8,11b,12,14-heptaazadibenzo[*de*,*hi*]naphthacene (**6**). The structure of **6** was supported by satisfactory elemental analysis, by the presence of NH-absorption and the absence of CN-absorption in the ir and appropriate pmr signals.

The preparation of **2d** in 52% yield involved the DMAP catalyzed reaction of **1a** with *N*-(5-amino-2,4-dimethylphenyl)trimethylacetamide (**8**). The latter compound was chosen as a substitute for the pyridine moiety in **2c** because the ring methyl substituents in **2d** would allow a ring closure of the proximate nitrile group to take place only between the nitrogens. Actually only one methyl group, (the 2-methyl of **2d**) is sufficient to prevent an undesired ring closure. However since 2,4-dimethylaniline (**9**) is commercially available and its conversion to 2,4-dimethyl-5-nitroaniline (**10**) is described in the literature [2] it seemed reasonable to investigate the conversion of the latter to *N*-(2,4-dimethyl-5-nitrophenyl)trimethylacetamide (**11**) with subsequent reduction of **8**. This route proved to be feasible. Thus refluxing **10** with trimethylacetyl chloride in pyridine for 1.25 hours gave a

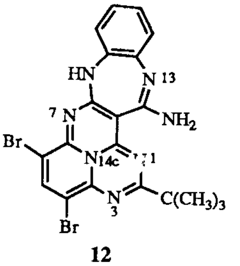
Figure 1



97% yield of *N*-(2,4-dimethyl-5-nitrophenyl)trimethylacetamide (**11**). Catalytic hydrogenation of **11** using 10% palladium on carbon gave **8** in 95% yield.

The ring closure of **1a** with **7** to give **3** prompted us to wonder about the possibility of a reaction of **1a** with *o*-phenylenediamine, the ring closure step forming a 7-membered ring. This turned out to be the case but the reaction required two steps. Thus refluxing **1a** with *o*-phenylenediamine in chloroform for about 0.5 hour in the presence of DMAP gave 5-*N*-(2-aminophenyl)amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2e**) in 64% yield. Ring closure to 14-amino-4,6-dibromo-2-*t*-butyl-8*H*-1,3,7,8,13,14c-hexaazabenzo[4,5]cyclohepta-[1,2-*a*]phenalene (**12**) in 58% yield was accomplished by by refluxing **2e** in *o*-dichlorobenzene in the presence of DMAP for 3 hours. The structure of **12** was supported by satisfactory elemental analysis, by the presence of NH absorption and the absence of CN absorption in the ir and appropriate pmr signals.

Figure 2



12

EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting point bath and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 1600 spectrophotometer. The pmr spectra were determined on Varian EM-360 and EM-390 spectrometers using TMS as an internal reference. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. All evaporations were carried out on a rotary evaporator at reduced pressure.

Silica gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical Inc. 2,4-dimethylaniline and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich Chemical Company.

7,9-Dibromo-2-*t*-butyl-4-cyano-5-*p*-toluidino-1,3,6,9b-tetraazaphenalene (**2b**).

A stirred solution of 3.0 g (0.0046 mole) of **1a** [3], 1.17 g (0.011

mole) of *p*-toluidine, 1.65 g (0.014 mole) of DMAP and 24 ml of chloroform was refluxed for 21 hours and filtered at the boil. The collected solids after washing successively with a little chloroform and carbon tetrachloride were allowed to air dry, 1.66 g (71%), mp >300°. Recrystallization from *N,N*-dimethylformamide (DMF) gave purplish-red crystals, mp >300°; ir Nujol): 3302 (NH), 2221 (CN) cm^{-1}; pmr (deuteriochloroform and trifluoroacetic acid): δ 1.39 (s, 9H, *t*-Bu), 2.37 (s, 3H, CH_3), 7.09 (d, J = 8 Hz, 2H, benzene H_2 and H_6), 7.49 (d, J = 8 Hz, 2H, benzene H_3 and H_5), 8.07 (s, 1H, H_8).

Anal. Calcd. for $C_{21}H_{18}Br_2N_6$: C, 49.05; H, 3.53; N, 16.34. Found: C, 49.10; H, 3.53; N, 16.37.

4,6-Dibromo-2-*t*-butyl-8,13-dihydro-13-imino-11-methyl-1,3,7,8,13c-pentaazabenzo[*de*]naphthacene (**4**).

A thin slurry of 2.43 g (0.018 mole) of anhydrous aluminum chloride, 0.12 ml of concentrated hydrochloric acid and 30 ml of chlorobenzene was stirred at room temperature for 5 minutes and then 1.17 g (0.0023 mole) of **2b** was added in one portion. The mixture was stirred for a few minutes more at room temperature, refluxed for 55 minutes and then cooled to room temperature. About 30 g of crushed ice was added to the gummy residue after the chlorobenzene was decanted away. The gum was broken up with a spatula and the mixture was stirred for 45 minutes. The collected solids were washed with distilled water and after oven drying overnight (60°) were slurried in 30 ml of methanol. The mixture which turned from red to tan upon adding 4 ml of triethylamine was stirred for 30 minutes at room temperature, filtered, washed well with methanol and oven dried at 100° for 3 hours, 1.0 g (85%), mp >330°. Recrystallization from DMF gave golden needles, mp >330°; ir (Nujol): 3462 (NH), 2500-2000 (transparent) cm^{-1}; pmr (deuteriochloroform and trifluoroacetic acid): δ 1.32 (s, 9H, *t*-Bu), 2.40 (s, 3H, CH_3), 7.15-7.74 (m, 3H, H_9, H_{10}, H_{12}), 8.10 (s, 1H, H_5).

Anal. Calcd. for $C_{21}H_{18}Br_2N_6$: C, 49.05; H, 3.53; N, 16.34. Found: C, 48.78; H, 3.82; N, 16.31.

7,9-Dibromo-2-*t*-butyl-4-cyano-5*N*-(2,4-dimethyl-5-trimethylacetamidophenyl)amino-1,3,6,9b-tetraazaphenalene (**2d**).

A stirred solution of 3.96 g (0.018 mole) of *N*-(5-amino-2,4-dimethylphenyl)trimethylacetamide, 3.30 g (0.027 mole) of DMAP, 5.94 g (0.009 mole) of **1a** and 48 ml of chloroform was refluxed for 2 hours and then filtered hot. The filter cake was washed with a little chloroform and then with carbon tetrachloride. The oven dried (60°) filter-cake weighed 2.93 g (52%), mp 292-294° dec. Recrystallization from 2-methoxy-ethanol gave purple crystals mp 292-294°; ir (Nujol): 3405, 3283 (NH), 2204 (CN), 1657 (C = O) cm^{-1}; pmr: (deuteriochloroform, trifluoroacetic acid, and deuterium oxide): δ 1.27 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 1.92 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 7.04 (s, 1H, phenyl-H_6), 7.84 (s, 1H, phenyl-H_3), 8.56 (s, 1H, H_8).

Anal. Calcd. for $C_{27}H_{29}Br_2N_7O$: C, 51.69; H, 4.66; N, 15.63. Found: C, 51.82; H, 4.72; N, 15.45.

9,11-Dibromo-2,13-di-*t*-butyl-4,6-dimethyl-7-*H*-1,3,7,8,11b,12,14-heptaazadibenzo[*de,hi*]naphthacene (**6**).

A stirred solution of 1.25 g (0.002 mole) of **2d** in 80 ml of chlorobenzene at 110° was treated with 2.12 g (0.016 mole) of aluminum chloride. The mixture was refluxed for 1 hour, cooled to room temperature and the chlorobenzene was decanted away. The residue was stirred with about 30 g of crushed ice, filtered, washed with distilled water (4 x 20 ml) and suctioned damp-dry. The filter cake was washed repeatedly with ether and oven dried at 60°. A stirred slurry of the rust-colored solid in 25 ml of methanol was treated with 3 ml of triethylamine and the mixture was allowed to stir for 1.5 hours. Collection of the solids by suction filtration followed by washing of the filter cake with methanol gave 0.74 g (61%), mp >325°. Recrystallization from *N,N*-dimethylacetamide gave bronze crystals, mp >325°; ir (Nujol): 3374 (NH) cm^{-1}; pmr (deuteriochloroform and trifluoroacetic acid): δ 1.40 (s, 9H, *t*-Bu), 1.53 (s, 9H, *t*-Bu), 2.48 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 7.84 (s, 1H, H_5), 8.17 (s, 1H, H_{10}).

Anal. Calcd. for $C_{27}H_{27}Br_2N_7$: C, 53.21; H, 4.47; N, 16.09. Found: C, 53.43; H, 4.47; N, 16.06.

N-(2,4-Dimethyl-5-nitrophenyl)trimethylacetamide (**11**).

A stirred solution of 10.0 g (0.06 mole) of 2,4-dimethyl-5-nitroaniline [2] in 50 ml of dry pyridine was treated with 7.35 g (0.06 mole) of trimethylacetyl chloride and the mixture was refluxed for 1.25 hours. About 22 ml of pyridine was evaporated and the cooled residue was poured into 100 ml of water. The mixture was stirred for 40 minutes, filtered and the filter cake was washed well with water, 14.5 g (97%) (air-dried), mp 116-119°. Recrystallization from toluene gave cream needles, mp 115-117°; ir (Nujol): 3284 (NH), 1648 (C=O), 1522, 1338 (NO_2) cm^{-1}; pmr (deuteriochloroform): δ 1.34 (s, 9H, *t*-Bu), 2.24 (s, 3H, 2-CH_3), 2.52 (s, 3H, 4-CH_3), 7.12 (s, 1H, H_3), 7.54 (s, broad, 1H, NH), 8.53 (s, 1H, H_6).

Anal. Calcd. for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.20. Found: C, 62.45; H, 7.26; N, 11.19.

N-(5-Amino-2,4-dimethylphenyl)trimethylacetamide (**8**).

A solution of 12.5 g of **11** in 250 ml of ethanol was added to a Parr hydrogenation bottle containing 1.0 g of 10% palladium on carbon catalyst. The bottle was purged with hydrogen several times and pressured to 50 psi. The mixture was shaken for 1.5 hours and the contents of the bottle was then filtered at room temperature and the filtrate was evaporated to dryness, 10.5 g (95%), mp 143-148°. Recrystallization from petroleum ether (120-140°) gave white crystals, mp 145-147°; ir (Nujol): 3433, 3332 (NH), 1645 (C = O) cm^{-1}; pmr (deuteriochloroform): δ 1.35 (s, 9H, *t*-Bu, 2.10 (s, 6H, 2 and 4-CH_3), 3.53 (s, broad, 2H, NH_2), 6.87 (s, 1H, H_6), 7.37 (s, broad, 2H, NH-CO and H_3).

Anal. Calcd. for $C_{13}H_{20}N_{20}$: C, 70.87; H, 9.15; N, 12.72. Found: C, 71.16; H, 9.21; N, 12.74.

5-*N*-(2-Aminophenyl)amino-7,9-dibromo-2-*t*-butyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2e**).

To a stirred solution of 0.65 g (0.006 mole) of *o*-phenylenediamine, 1.1 g of DMAP and 15 ml of chloroform (nitrogen atmosphere) was added 1.98 g (0.003 mole) of **1a**. A precipitate formed very quickly and after 5 minutes of reaction at ≈30°, 10 additional ml of chloroform was added. The mixture was then refluxed for 25 minutes and filtered at the boil. The filter cake was washed twice with small amounts of chloroform and oven dried at 60°, 0.98 g (64%), mp 283-285°. Recrystallization from *N,N*-dimethylacetamide/methanol gave the analytical sample, pink crystals, mp 295-296°; ir (Nujol): 3344, 3322 and 3236 (NH), 2217 (CN) cm^{-1}; pmr (DMSO-d_6): δ 1.17 (s, 9H, *t*-Bu), 6.53-7.12 (m, 4H, C_6H_4), 8.09 (s, 1H, H_8).

Anal. Calcd. for $C_{20}H_{17}Br_2N_7$: C, 46.62; H, 3.32; N, 19.03. Found: C, 46.80; H, 3.27; N, 19.31.

14-Amino-4,6-dibromo-2-*t*-butyl-8*H*-1,3,7,8,13,14c-hexaazabenzo-[4,5]cyclohepta[1,2-*a*]phenalene (**12**).

A stirred mixture of 0.60 g (0.0012 mole) of **2e**, 0.22 g (0.0018 mole) of DMAP and 8 ml of *o*-dichlorobenzene was refluxed for 3 hours. The collected solid was washed several times with ether and then recrystallized from chlorobenzene to give 0.33 g of a pink solid, mp 345-347° dec; (tlc chloroform-methanol/95:5 showed one spot); ir (Nujol): 3448, 3145 (NH), 2500-2000 no significant absorption; pmr (DMSO-d_6): δ 1.17 (s, 9H, *t*-Bu), 7.11-7.71 (m, 4H, H_9, H_{10}, H_{11}, H_{12}), 8.03 (s, 1H, H_5).

Anal. Calcd. for $C_{20}H_{17}Br_2N_7$: C, 46.62; H, 3.32; N, 19.03. Found: C, 46.79; H, 3.19; N, 19.36.

Acknowledgement.

Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

We owe special thanks to Dr. Kurt L. Loening, Nomenclature Director, Chemical Abstracts Service, for the naming and numbering of ring systems **3**, **4**, **5**, and **6**.

REFERENCES AND NOTES

[1] J. T. Shaw, M. F. Egler, V. S. Peciulis, R. Pustover, and W. G. Ruth, *J. Heterocyclic Chem.*, **27**, 1591 (1990).

[2] R. Gautron, French Patent 1,451,332 (1966); *Chem. Abstr.*, **66**, 105904p (1967).

[3] J. T. Shaw and M. C. Fair, *J. Heterocyclic Chem.*, **24**, 321 (1987).