DIAZABICYCLOALKANES WITH NITROGEN ATOMS IN NODAL POSITIONS.

13.* REACTIONS OF BENZO[b]-1,4-DIAZABICYCLO[2.2.2]OCTENE WITH ELECTROPHILES

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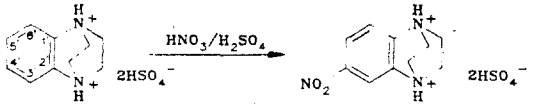
The reactions of electrophiles with benzo[b]-1,4-diazabicyclo[2.2.2]octene have been examined. Electrophilic substitution is found to take place in the aromatic ring under severe conditions, in the case of halogenation giving high yields. The structures of the electrophilic substitution products indicate that the heteroatoms have a m-directing influence.

It is known [2, 3] that benzo[b]quinuclidine is deactivated to a considerable extent toward electrophilic substitution as a result of the absence of conjugation between the free electron pair on the nitrogen and the π-electrons of the benzene ring. Benzo[b]-1,4-diazabicyclo[2.2.2]octene (I) contains two nitrogen atoms in nodal positions, and consequently, electrophilic substitution in the benzene ring should be even more strongly hindered. However, bearing in mind the attractiveness of this approach to the synthesis of benzo[b]-1,4-diazabicyclo[2.2.2]octenes substituted in the benzene ring, we have examined the behavior of (I) toward some electrophiles.

Treatment of the base (I) in acetonitrile with nitronium fluoroborate results in an exothermic reaction, probably as a result of the formation of an N-nitronium complex, from which the original (I) can be recovered. When the mixture is boiled with an excess of nitronium fluoroborate, extensive decomposition occurs, probably as a result of oxidative cleavage of the heterocycle. Compound (I) did not undergo sulfonation on boiling in chlorosulfuric acid, although benzo[b]quinuclidine reacts at 50°C [2]. No sulfonation took place on heating in sulfuric acid and oleum at 200°C for several hours, but no appreciable decomposition of (I) took place, suggesting the use of this medium for a study of the effects of other electrophiles.

Treatment of a solution of (I) in sulfuric acid with nitric acid at 130°C gave a mixture from which a low yield of a nitro-compound was isolated. From its mass and PMR spectra, this was assigned the structure 4'-nitrobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (II).



I II

The highest yields of (II) were obtained using a mixture of 93% sulfuric and 99% nitric acids. This composition of the nitrating mixture results in the greatest rate of nitration in numerous benzene derivatives [4]. Under these conditions, after heating for several hours, a product was isolated which, according to microcolumn liquid chromatography, consisted mainly of (I) and (II) in a ratio of 5:1. Further heating did not result in the accumulation of the nitro-compound (II) in the mixture, and the total amount of product isolated decreased, possible owing to cleavage of the heterocycle under the reaction conditions. For this reason, it was desirable to stop the reaction at an early stage, and isolate the nitro-compound together with substantial amounts of unreacted (I). The separation of the nitration product from the starting material was difficult, since they crystallize in equimolar ratio, as shown by liquid chromatography, PMR and IR spectroscopy. The co-crystallizate obtained can be

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TABLE 1. Benzo[b]-1,4-diazabicyclo[2.2.2]octenes

Compound	mp,* °C	R_f	IR spectrum, cm^{-1}				Found					Empirical formula	Calculated					Yield,‡ %
			stretching vibrations†		deformational vibrations		C, %	H, %	N, %	Br (I), %	M (mass spectrum)		C, %	H, %	N, %	Br (I), %	M	
			C—N	C—H (arom C—H)	CH_2	arom. C—H												
I·Br_2	195	0,10	1048	2961	1477, 845	794	37,3	3,8	8,7	49,9	—	$C_{10}H_{12}N_2 \cdot Br_2$	37,5	3,8	8,8	49,9	—	88
I·$2I_2$	158—160	0,08	1040	2942	1463, 833	824, 787, 758	18,0	1,7	3,9	(76,3)	—	$C_{10}H_{12}N_2 \cdot 2I_2$	18,0	1,8	4,2	(76,0)	—	97
I·II	87—112	0,13; 0,17	1048	(3013), 2972, 2951, 2886	1479, 820	802, 786, 750	65,3	6,1	19,1	—	—	$C_{10}H_{12}N_2 \cdot C_{10}H_{11}N_3O_2$	65,7	6,3	19,2	—	—	13
II	115—117	0,17	1048	(3020), 2981, 2954, 2886	1475, 820	802, 748	58,9	5,4	20,6	—	205	$C_{10}H_{11}N_3O_2$	58,5	5,4	20,5	—	205	60
III	117—121	0,19	1051	(3062), 2979, 2945, 2881	1478, 813	900, 841	50,1	4,6	11,9	33,0	238, 240	$C_{10}H_{11}BrN_2$	50,2	4,6	11,7	33,4	238, 240	37 (A), 0 (B)
IV	234—235	0,21	1041	(3064), 2971, 2943, 2885	1456, 811	864, 822	37,6	3,1	8,6	49,8	316, 318, 320	$C_{10}H_{10}Br_2N_2$	37,8	3,2	8,8	—	316, 318, 320	47 (A), 14 (B)
V	185—192	0,43	1042	(3050), 2968, 2940, 2877	1453, 833	868	30,3	2,1	7,3	60,6	396, 398	$C_{10}H_9Br_3N_2$	30,3	2,3	7,1	60,4	396, 398	4 (A), 26 (B)
VI	224—225	0,73	1050	2953, 2882	1459, 835	—	25,1	1,9	6,1	66,8	474, 476, 478	$C_{10}H_8Br_4N_2$	25,2	1,7	5,9	67,2	474, 476, 478	5 (A), 53 (B)
VII	160—161	0,16	1045	(3030), 2960, 2940, 2876	1473, 827	893, 807	41,6	3,9	9,9	(44,3)	286	$C_{10}H_{11}IN_2$	42,0	3,9	9,8	(44,4)	286	35
VIII	177—180	0,22	1048	(3043), 2963, 2950, 2880	1455, 817	855, 832	29,5	2,3	7,0	(61,2)	412	$C_{10}H_{10}I_2N_2$	29,2	2,4	6,8	(61,6)	412	67
IX	179—181	0,50	1054	(3061), 2980, 2950, 2887	1463, 834	850	21,9	1,6	5,0	(70,7)	538	$C_{10}H_9I_3N_2$	22,3	1,7	5,2	(70,8)	538	5
X	220—221	0,87	1042	2938, 2872	1453, 828	—	18,5	1,1	3,9	(76,6)	664	$C_{10}H_8I_4N_2$	18,1	1,2	4,2	(76,5)	664	0,4

*Compounds I·Br_2, I·$2I_2$, and (VIII-X) with decomposition; I·$2I_2$ and (IV-VI) in a capillary.
†For (I·II) and (II), ν_{N-O} 1529 cm^{-1}.
‡The yield of (I·II) is calculated on (I) consumed.

TABLE 2. PMR Spectra of Benzo[b]-1,4,-diazabicyclo[2.2.2]octenes Substituted in the Aromatic Ring* δ, ppm

Compound	PMR Spectra in neutral media				PMR Spectra in acid media**				Δδ***, ppm		
	aromatic protons (J, Hz)			ethylene bridge protons (sym.m)	aromatic protons (J, Hz)			ethylene bridge protons (sym.m)			
	3'-H	6'-H	5'-H		3'-H	6'-H	5'-H		3'-H	6'-H	5'-H
II	7,88 d (2,6)	7,35 d (8,5)	8,20 dd	2,5—3,5	8,32 d (2,6)	7,83 d (8,5)	8,44 dd	3,2—4,0	0,44	0,48	0,24
III	7,28 d (2,3)	7,05 d (8,1)	7,44 dd	2,4—3,2	7,68 s	7,50 d (8,0)	7,73 d (8,0)	3,1—3,9	0,40	0,45	0,29
IV	7,44 s		—	2,4—3,2	7,90 s		—	3,1—3,9	0,44		—
V	7,52 s		—	2,4—3,3	8,04 s		—	3,1—4,0	0,52		—
VI	—	—	—	2,5—3,3	—	—	—	2,7—3,5	—	—	—
VII	7,47 d (1,9)	6,93 d (8,1)	7,63 dd	2,4—3,2	7,88 s	7,37 d (7,4)	7,92 d (7,4)	3,0—3,8	0,41	0,44	0,29
VIII	7,66 s		—	2,4—3,2	8,07 s		—	3,0—3,9	0,41		—
IX	7,78 s		—	2,4—3,2	8,26 s		—	3,1—4,0	0,48		—
X	—	—	—	2,4—3,1	—	—	—	2,5—3,3	—	—	—

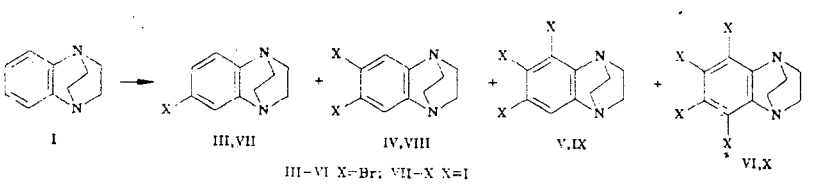
*Spectra taken at 90 MHz in DMFA-D_{17}, ratios of signal intensities agree with the proposed structures.
**Acidity was attained by adding CF_3COOH to 3%; further increase in acid concentration did not lead to a change in in CS.
***Downfield shift of the aromatic protons during protonation of the nitrogen atom.

separated by preparative TLC. Losses on purification reduce the overall yield to 1.5, or 8% calculated on the (I) reacted.

The reaction of (I) with bromine or iodine affords the molecular complexes $I \cdot Br_2$ and $I \cdot 2I_2$, which on heating to 150°C did not give ring-halogenated products, in accordance with an earlier report [2].

We have been able to brominate (I) using dibromocyanuric acid in oleum [5, 6]. When this reaction was carried out at 130°C, a mixture of bromination products of benzo[b]-1,4-diazabicyclo[2.2.2]octene (III-VI) was obtained, the relative amounts of which were dependent on the amount of brominating agent and the reaction time. The principal components of these mixtures were readily separable by crystallization, and the residual mixture could be separated chromatographically. The use of an equivalent amount of dibromoisocyanuric acid resulted in the preferential formation of the dibromo compound (IV), and the use of two equivalents gave mostly the exhaustive bromination product (VI). The mono- and tribromo compounds (III) and (V) were isolated as minor components from the reaction mixture by TLC. Bromination was not complicated by side reactions, and the overall yield of bromination products reached 93%.

Examination of the structures of the compounds showed that bromination initially takes place in the position meta- to the heteroatom, but this does not deactivate the aromatic ring to further electrophilic substitution. This results in the successive substitution, initially in the other meta-position to the nitrogen atom, and subsequently, to successive substitution in the ortho-positions.



The use of a powerful iodinating agent, namely iodine in oleum at 150°C, also results in successive substitution in the aromatic ring of benzo[b]-1,4-diazabicyclo[2.2.2]octene. As in bromination, monosubstitution by iodine does not decrease the ability of the aromatic ring to undergo further substitution. Consequently, the diiodo compound (VIII) is formed. For this reason, in order to obtain sufficient amounts of the mono-iodo compound (VII) it is necessary to use a twofold deficiency of iodine, and to separate the mixture of (I) and

(VII) obtained by preparative TLC. Further substitution in the free positions in (VII) takes place with great difficulty, and even when an excess of iodine was used the tri- and tetraiodo compounds (IX and X) were obtained in low yields. All the iodination products were separable by preparative TLC.

In the mass spectra of (II-X) (Table 1), in addition to the molecular ion, peaks were present for the fragments $[M - 28]^{+\cdot}$, corresponding to cleavage of the ethylene bridges. The molecular ions for the bromination products of (I) were seen as groups of peaks, the positions and intensities of which were in accordance with the amounts and natural content of ^{79}Br and ^{81}Br isotopes in the molecule.

In the IR spectra of the benzo[b]-1,4-diazabicyclo[2.2.2]octene derivatives, vibrations were present characteristic of the diazabicyclo[2.2.2]octane fragment [7], manifested as the strongest absorption bands at 2981-2876 and 1054-1040 cm^{-1} (C—N stretching and skeletal vibrations of the 1,4-diazabicyclo[2.2.2]octane fragment) and at 1479-1453 and 845-811 cm^{-1} (deformational vibrations of the CH_2 group). In addition, in compounds containing aromatic protons, weaker signals were seen at 3064-3013 and 900-748 cm^{-1} corresponding to stretching and deformational vibrations of the aromatic ring C—H.

In the PMR spectra of (II-X) (Table 2), symmetrical multiplets were present in 2.4-3.5 ppm, corresponding to the eight protons of the ethylene bridges. The signals were shifted by 0.2-0.7 ppm to lower field when the nitrogens were protonated by adding trifluoroacetic acid. The signals for the aromatic protons in (II), (III), and (VII) corresponded to 1',2', 4'-trisubstitution in the benzene ring, the 5' and 6' protons having coupling constants of 8.1-8.5 Hz, and those in positions 3' and 5', of 1.9-2.6 Hz, characteristic of ortho- and meta-positions for the protons, respectively. When the nitrogens were protonated, the signals for the aromatic protons were shifted to lower field. For the 3' and 6' (protons, in the ortho-positions to the protonation center, this shift was ~0.5 ppm, which is greater by a factor of two than the shifts for the signals for the meta-located 5' protons. Similar observations have been made by Mikhlina et al. [2] in a study of the structures of substituted benzo[b]quinuclidines. Hence, a comparison of the PMR spectra in neutral and acidic media is a satisfactorily general method for establishing the positions of substituents in the aromatic ring in these heterocyclic systems.

The signals for the aromatic protons in (IV), (V), (VIII), and (IX) are seen as singlets at 7.44-7.78 ppm, which in acidic media are shifted to lower field by 0.41-0.52 ppm. A shift of this magnitude is characteristic only of protons ortho- to nitrogen, confirming the postulated structures. Study of the nature of the $^{13}C—H$ satellites in the PMR spectra at 200 MHz for (IV) and (VIII) shows that the coupling constants for the aromatic protons in these compounds approaches zero, in agreement with the relative para-disposition of the protons in the aromatic ring.

EXPERIMENTAL

The IR spectra of the compounds were obtained on a UR-20 instrument in KBr disks, and UV spectra on a Specord UV-VIS in pentane. PMR spectra were obtained on Bruker HX-90 and WP-200 s, y spectrometers, internal standard TMS, δ scale. Mass spectra were obtained on a Finnigan MAT-8200. The quantitative compositions of the reaction mixtures were measured by reversed-phase chromatography (LC) on Lichrosorb RP-18 as carrier, particle size 5 μm, diameter of micro-column 2 mm, height 50 mm, on a Milikhrom chromatograph, eluent 0.1 M acetate buffer (pH 5.0) in 60% methanol. Preparative chromatography was carried out on thin layers of silica gel on 35 × 70 cm plates in the system chloroform—ethanol, 20:1, the compounds being eluted from the silica gel with a mixture of chloroform and methanol (5:1). TLC was carried out on Silufol UV-254 plates in the system chloroform—ethanol (20:1). Compounds (II-VIII) were sublimed in vacuo at 100-170°C (0.1 mm).

Benzo[b]-1,4-diazabicyclo[2.2.2]octene (I) was obtained as described in [8]. To prevent a violent reaction when dissolving in acids, the (I) was used in a coarsely crystalline state.

Complex of Benzo[b]-1,4-diazabicyclo[2.2.2]octene with Bromine (I•Br_2). This was obtained by treating a solution of 0.2 g (1.25 mmole) of (I) in 8 ml of ether with 0.2 g (1.25 mmole) of bromine over ten minutes with sitrring. The solid was filtered off, washed with ether, and dried in vacuo to give 0.35 g of a yellow solid. PMR spectrum (90 MHz, in DMFA-D_7): 7.53 (4H, s, arom. protons), 3.8-3.0 ppm (8H, sym. m., CH_2).

Complex of Benzo[b]-1,4-diazabicyclo[2.2.2]octene with Iodine ($I \cdot 2I_2$). This was obtained by mixing solutions of 0.32 g (2 mmole) of (I) in 30 ml of ether and 1.02 g (4 mmole) of iodine in 20 ml of ether. The mixture was kept for 12 h, then filtered, washed with ether, and dried in vacuo. Yield 1.3 g of a reddish-orange solid. PMR spectrum (90 MHz, in DMFA-D_7): 7.55 (4H, s, arom. protons), 4.0-3.1 ppm (8H, sym. m., CH_2).

Cocrystallizate of Benzo[b]-1,4-diazabicyclo[2.2.2]octene and 4'-Nitrobenzo[1'2'-b]-1,4-diazabicyclo[2.2.2]octene (I•II). To 160 ml of 93% sulfuric acid (d 1.83) frozen in liquid nitrogen was added 64 g (0.4 mole) of (I), and the mixture stirred with gradual heating to 100°C, until all the base had dissolved. To the solution initially, and after 1, 2, and 3 h with heating at 130°C were added with care and stirring 15 ml portions of fuming nitric acid (d 1.51). After ~~four~~ h had elapsed, the mixture was cooled, carefully poured into an equal volume of water, and air blown through to remove oxides of nitrogen. The mixture was then neutralized with 700 ml of 25% ammonia with stirring and constant cooling to 0°C, the ammonia being carefully introduced through a capillary immersed in the reaction mixture. The nitration products and unreacted base were extracted with 4 × 300 ml of ether, and the extract dried over $MgSO_4$ and evaporated to dryness. The solid residue was boiled for several minutes with 40 ml of acetone, gradually cooled to 15°C, filtered, and the crystalline solids washed three times on the filter with 12 ml portions of acetone to give 51.5 g of the starting material (I), mp 126-129°C, containing, according to TLC, a small amount (0.8%) of the nitro-compound (II). The nitration product separated as a cocrystallizate with the starting material on evaporation of the mother liquors, and was recrystallized from 120 ml of light petroleum (bp 70-100°C) to give 3.66 g of a yellow crystalline solid. PMR spectrum (90 MHz, in $CDCl_3$): 8.18 (1H, d.d, 5'-H arom.); 8.03 (1H, d, J = 2.6 Hz, 3'-H arom.); 7.32 (1H, d, J = 8.5 Hz, 6'-H arom.), 7.23 (4H, s, arom. protons), 3.5-2.5 ppm (16H, m, CH_2). Evaporation of the mother liquors gave 2.0 g of (I), mp 126-129°C.

4'-Nitrobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (II) was separated by TLC from 1.2 g of the cocrystallizate (I•II). The fraction with Rf 0.2-0.4 gave 0.5 g of (I), mp 127-129°C. Compound (II) was extracted from the fraction with Rf 0.4-0.5, and recrystallized from light petroleum (bp 70-100°C), yield 0.4 g, as a yellow crystalline solid in the form of needles. UV spectrum λ_{max}, nm (log ε): 216 (4.02), 263 (3.98).

4'Bromo, 4',5'-Dibromo, 3',4',5'-Tribromo-, and 3',4',5',6'-Tetrabromobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (III-VI). A. To 20 ml of oleum (d 1.91) frozen in liquid nitrogen was added 1.28 g (8 mmole) of (I), and the mixture gradually heated to 70°C, until all the base had dissolved. To this solution was added with stirring in small portions 2.4 g (8.4 mmole) of dibromoisocyanuric acid. The mixture was maintained at 130-140°C on an oil bath for 6 h. Water (20 ml) was then added with cooling to 0°C with constant stirring, followed by the careful addition of 25% ammonia (100 ml), through a capillary immersed in the reaction mixture. The bromination products were extracted with 5 × 100 ml of ether, the extract dried over $MgSO_4$, and evaporated to dryness. The resulting mixture of bromides (2.5 g) was dissolved in the minimum amount (~150 ml) of boiling light petroleum (bp 70-100°C) and cooled whereupon the major part of (IV) crystallized as prisms (1.0 g). The mother liquors were evaporated, and the residue separated by TLC and recrystallized from light petroleum (bp 70-100°C). Compounds (III-VI) were extracted from the fractions with Rf 0.4-0.5, 0.5-0.6, 0.6-0.7, and 0.7-0.8 (Table 1).

B. All operations were carried out as in method A, with 4.8 g (16.7 mmole) of dibromoisocyanuric acid, and the reaction mixture was kept for 12 h. The bromination products (3.5 g) were dissolved in the minimum amount (~350 ml) of boiling light petroleum (bp 70-100°C). Crystallization gave 1.7 g of (VI). The remaining compounds were extracted from the mother liquors by TLC.

4'-Iodobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (VII). To a solution of 1.28 g (8 mmole) of (I) in 10 ml of 24% oleum, prepared as described above, was added with stirring 0.51 g (2 mmole) of iodine. The mixture was kept at 140°C on the oil bath for 4 h, then 10 ml of water was added with constant stirring and cooling to 0°C, followed by 50 ml of 25% ammonia, carefully introduced through a capillary immersed in the reaction mixture. The iodination product together with unreacted (I) were extracted with 3 × 80 ml of ether, and the extract dried over $MgSO_4$ and evaporated to dryness. The resulting mixture was separated by TLC. The fraction with Rf 0.2-0.3 gave 0.87 g of (I), mp 127-129°C. From the fraction with Rf 0.3-0.4, following recrystallization from light petroleum (bp 70-100°C), there was obtained 0.4 g of (VII) as colorless needles.

4',5'-Diiodo, 3',4',5'-Triiodo-, and 3',4',5',6'-Tetraiodobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (VIII-X). To a solution of 0.64 g (4 mmole) of (I) in 10 ml of 24% oleum was added with stirring 3.0 g (11.8 mmole) of iodine, and the mixture kept at 150°C for 3 h. The preparation of the solution and its neutralization were carried out as described above. Excess iodine was removed by adding 3 g of $Na_2S_2O_3 \cdot 5H_2O$, the mixture stirred for 5 min until decolorized, and diluted with 100 ml of water. The iodination products were filtered off, washed with 50 ml of 3% $Na_2S_2O_3$ solution followed by water, and dried in vacuo to give 1.43 g of a mixture consisting principally of (VIII-X). This was separated by TLC, and the separate components recrystallized from a mixture of chloroform and light petroleum (bp 70-100°C). Compounds (VIII-X) were extracted from the fractions with R_f 0.4-0.5, 0.5-0.6, and 0.8-0.9.

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CYCLOTRIMERIZATION OF THIOCYANIC ACID IN ORGANIC SOLVENTS

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Thiocyanic acid in organic solvents (i-PrOH Bu_2O, AcOH, dioxane) trimerizes to form 1,3,5-trimercapto-sym-triazine.

When thiocyanic acid (TCA) is heated in aqueous medium, the formation of 5-amino-1,2,4-dithiazol-3-thione (I) takes place and hydrogen cyanide is evolved [1]. The purpose of our work was to study the conversion of TCA in organic solvents.

We carried out the reaction in i-PrOH, AcOH, Bu_2O, and dioxane. As starting material, we used the pyridinium salt of TCA, which is readily soluble in organic solvents. Heating the solution of pyridinium thiocyanate in organic solvent in the presence of sulfuric acid led to the formation of a yellow powder (II). The UV spectra of products obtained in different solvents were identical and differed from the UV spectrum of compound I. Material II did not melt up to 300°C, dissolved readily in sulfolane and pyridine but poorly in dioxane and benzene. The compound was soluble in aqueous solutions of inorganic acids and bases. The IR spectrum of the compound contained absorption bands characteristic of the triazine ring: 680, 1020, 1400 (C—N), 840, 920, and 1570 (C=N) as well as absorption bands in the 1315 cm^{-1} region (S—C=N). The molecular mass of the compound, 177, was determined from an analysis of the mass spectrum. The data listed, the PMR spectrum, and also the elementary analysis of the compound indicate that under our experimental conditions, TCA undergoes a cyclotrimerization to form 1,3,5-trimercapto-sym-triazine, II. This conclusion was confirmed by a reverse synthesis [2].

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