CHEMISTRY OF ETHYLENEIMINE

X.* PMR SPECTRA OF SUBSTITUTED 1,3-DIAZABICYCLO[3.1.0]HEXANES

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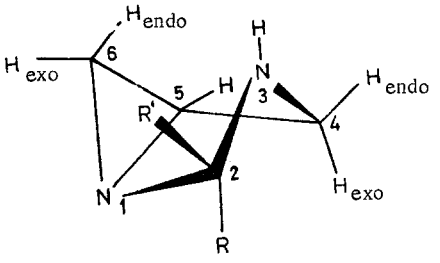
The configuration of 2-substituted 1,3-diazabicyclo[3.1.0]hexanes was studied by means of PMR spectroscopy. When R ≠ R', it was proved that they exist in endo and exo forms, and equilibrium between both forms was detected in solutions in the case of 2-aryl-substituted derivatives. Conversion of the endo to the exo form is observed in crystals under the influence of x-ray irradiation.

The present communication is devoted to a more detailed study of the stereochemistry of new bicyclic systems – substituted 1,3-diazabicyclo[3.1.0]hexanes [2, 3] – by means of PMR spectroscopy.



The parameters of the PMR spectra of 1,3-diazabicyclo[3.1.0]hexane (I) and its substituted derivatives are presented in Table 1. The PMR spectrum of unsubstituted bicyclic I is analyzed relatively simply. The H_6-exo and H_6-endo protons resonate at strongest field, and their spin–spin coupling constants (SSCC) are extremely characteristic for 1,2-disubstituted ethyleneimines ($^2J < 0.5$ Hz and $^3J_{cis} > {}^3J_{trans}$ [4]). The typical values of the chemical shifts for the remaining protons and the application of double-resonance methods (collapse and INDOR) make it possible to make further assignments. The theoretical PMR spectrum of I calculated with a computer coincides satisfactoryly with the experimental spectrum (Fig. 1 and Table 1).

Signals corresponding to two configurational isomers that differ with respect to the orientation of the substituents in the 2 position and their relative percentages in the mixture are detected in the spectra of all of the unsymmetrically substituted 1,3-diazabicyclo[3.1.0]hexanes. The SSCC for both isomers differ only slightly from the values in the spectrum of unsubstituted I. It can therefore be asserted that the primary conformation of the molecule remains unchanged both in the endo and exo forms when a substituent is introduced. The $H_{endo}-C_4-C_5-H$ (70°) and $H_{exo}-C_4-C_5-H$ (50°) dihedral angles calculated from the Karplus equation [5] correspond to a skew boat conformation for the investigated bicyclic compounds. This

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TABLE 1. Parameters of the PMR Spectra of 1,3-Diazabicyclo[3.1.0]hexanes

Compound	R	R′	Chemical shifts, τ, ppm								Spin–spin coupling constants,* Hz				
			6-exo	6-endo	5	4-endo	4-exo	NH	R	R′	6-exo, 5	6-endo, 5	4,4	4-exo, 5	4-endo, 6-exo
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
I	H	H	8,66	8,92	7,85	6,97	7,33	7,3	6,64	6,44	4,9	3,1	−11,4	3,1	1,0
II	CH_3	CH_3	8,69	9,04	7,86	6,95	7,10	8,5	8,83	8,89	4,9	2,9	−11,4	2,9	1,0
III	$C_6H_5CH_2$	$C_6H_5CH_2$	8,65	9,15	7,90	7,15	7,50	8,4	7,32 (CH_2)	7,32 (CH_2)	4,7	3,0	−11,3	3,1	1,1
IV	—$(CH_2)_4$—		8,71	8,99	7,88	7,00			2,85 (C_6H_5)	2,85 (C_6H_5)					
V	—$(CH_2)_5$—		8,70	9,05	7,86	7,00	7,25	8,1	8,0—8,5	8,0—8,5	4,8	3,0	−11,7	3,0	1,1
VIA†	H	CH_3	8,81	8,89	7,85	6,97	7,10	8,2	8,3—8,7	8,3—8,7	4,8	3,0	−11,5	2,9	1,0
VIB	CH_3	H	8,62	8,98	7,85	6,99	7,20	8,5	6,20	8,88	4,6	3,0	−11,6	3,0	1,1
VIIA	H	C_2H_5	—	—	7,92	6,97	7,20	8,5	8,99	6,22	4,6	3,0	−11,6	3,0	1,1
VIIB	C_2H_5	H	—	—	7,92	7,01	7,21	8,3	6,47	—	—	—	−11,6	2,8	1,0
VIIIA	H	$C_6H_4NO_2$-*p*	8,62	8,94	7,60	6,70	7,21	8,3	—	6,57	—	—	−11,6	2,8	1,0
							6,88	8,3	5,18	2,32	4,7	3,0	−12,0	3,0	1,1
VIIIB	$C_6H_4NO_2$-*p*	H	8,37	8,80	7,70	6,90				2,00					
							7,38	8,3	2,44	5,23	4,8	3,0	−12,0	3,0	1,1
IXA	H	C_6H_4Br-*p*	8,65	8,97	7,66	6,81			1,98						
IXB	C_6H_4Br-*p*	H	8,42	8,87	7,75	6,95	7,01	8,0	5,24	2,65	4,8	2,9	−11,6	2,8	1,0
XA	H	C_6H_4Cl-*p*	8,68	8,97	7,65	6,80	7,33	8,0	2,65	5,33	4,7	3,0	−11,6	2,9	1,0
							7,00	7,8	5,27	2,55	4,6	2,9	−11,4	2,9	1,2
XB	C_6H_4Cl-*p*	H	8,46	8,89	7,75	6,95				2,83					
							7,32	7,8	2,65	5,36	4,5	3,0	−11,4	2,9	1,2
XIA	H	C_6H_4Cl-*m*	8,62	8,93	7,65	6,80			2,80						
XIB	C_6H_4Cl-*m*	H	8,41	8,85	7,72	6,97	7,00	8,2	5,20	2,5—2,8	4,8	2,9	−11,7	3,0	1,0
XIIA	H	C_6H_4F-*p*	8,70	8,94	7,71	6,86	7,29	8,2	2,5—2,8	5,30	4,7	2,9	−11,7	2,9	1,0
XIIB	C_6H_4F-*p*	H	8,49	8,90	7,80	7,03	7,06	7,7	5,25	2,51	4,7	3,0	−11,6	3,0	0,9
							7,33	7,7	2,60	5,33	4,7	3,0	−11,6	3,0	0,9
XIIIA	H	C_6H_5	8,66	8,94	7,65	6,85			3,12						
XIIIB	C_6H_5	H	8,40	8,81	7,75	6,95	7,01	8,2	5,16	2,5—2,9	4,6	2,8	−11,4	2,8	1,0
XIVA	H	$C_6H_4CH_3$-*p*	8,69	8,98	7,68	6,88	7,26	8,2	2,5—2,9	5,23	4,7	2,8	−11,4	2,8	1,0
							7,02	8,2	5,24	7,71 (CH_3)	4,6	2,9	−11,4	2,8	1,0
XIVB	$C_6H_4CH_3$-*p*	H	8,50	8,90	7,75	7,01				2,73 (C_6H_4) 2,95					
							7,31	8,2	7,71 (CH_3)	5,32	4,6	3,0	−11,5	2,9	1,1
XVA	H	$C_6H_4OCH_3$-*p*	8,71	8,97	7,75	6,92			2,73 (C_6H_4) 2,95						
							7,10	7,9	5,24	6,34 (OCH_3)	4,7	2,9	−11,8	2,8	1,0
XVB	$C_6H_4OCH_3$-*p*	H	8,52	8,92	7,83	7,05				2,73 (C_6H_4) 3,30					
							7,34	7,9	6,34 (OCH_3)	5,39	4,7	3,0	−11,7	2,8	1,0
XVIA	H	$C_6H_4N(CH_3)_2$-*p*	8,71	8,98	7,75	6,88			2,67 (C_6H_4) 3,32						
							7,06	8,4	5,30	7,14 (NCH_3)$_2$	4,6	2,9	−11,6	2,9	1,1
XVIB	$C_6H_4N(CH_3)_2$-*p*	H	8,51	8,90	7,82	7,04				2,81 (C_6H_4) 3,49					
							7,31	8,4	7,08 (NCH_3)	5,39	4,6	2,9	−11,6	2,9	1,2
XVIIA	H	$C_6H_5CH{=}CH$	8,72	8,98	7,79	6,96			2,75 (C_6H_4) 3,49						
							7,14	8,1	5,65	3,92 (α-H)	4,6	3,0	−11,5	3,0	1,1
XVIIB	$C_6H_5CH{=}CH$	H	8,58	8,85	7,81	7,08				3,36 (β-H) 2,62—2,9 (C_6H_5)					
							7,28	8,1	3,92 (α-H)	5,72	4,6	3,0	−11,5	3,0	1,0
XVIIIA	H	2-Furyl	8,66	8,55	7,74	6,87			3,36 (β-H) 2,6—2,9 (C_6H_5)						
							7,14	7,7	5,29	3,87 (3′-H) 3,77 (4′-H)	4,9	3,0	−11,4	2,9	1,2

TABLE 1. (continued)

Compound	R	R'	Chemical shifts, τ, ppm								Spin-spin coupling constants, * Hz				
			6-exo	6-endo	5	4-endo	4-exo	NH	R	R'	6-exo, 5	6-endo, 5	4,4	4-exo, 5	4-endo, 6-exo
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
XVIIIB	2-Furyl	H	8,48	8,81	7,78	6,97	7,14	7,7	3,87 (3′-H) 3,77 (4′-H) 2,75 (5′-H)	2,75 (5′-H) 5,32	4,9	3,1	−11,4	3,0	1,2
XIXA	CH_3	CH_2CH_3	8,72	8,90	7,90	7,01	7,11	8,2	8,96	9,04 (CH_3) 8,7 (CH_2)	4,5	2,8	−11,5	2,9	1,0
XIXB	CH_2CH_3	CH_3	8,72	8,90	7,90	7,01	7,14	8,2	9,04 (CH_3) 8,7 (CH_2)	8,96	4,5	2,8	−11,6	2,8	1,1
XXA	CH_3	$C_6H_4NO_2$-*p*	8,50	9,18	7,50	6,77	6,80	8,2	8,61	2,31 (C_6H_4) 1,88 (C_6H_4)	4,8	3,0	−11,4	2,9	1,1
XXB	$C_6H_4NO_2$-*p*	CH_3	8,40	8,78	7,80	7,00	7,05	8,2	2,31 (C_6H_4) 1,88	8,64	4,8	3,0	−11,4	3,0	1,0
XXIA	CH_3	C_6H_5	8,58	9,23	7,68	6,90	6,90	8,5	8,68	2,2—2,9	4,6	2,9	−11,6	2,9	1,1
XXIB	C_6H_5	CH_3	8,58	8,88	7,80	7,03	7,30	8,5	2,2—2,9	8,68	4,6	2,9	−11,5	2,9	1,0
XXIIA	CH_3	$CH_2C_6H_5$	8,67	9,04	7,83	7,01	7,26	8.5	9,00	7,35 (CH_2) 2,8 (C_6H_5)	4,9	3,1	−11,5	3,0	0,9
XXIIB	$CH_2C_6H_5$	CH_3	8,67	9,04	7,88	7,03	7,27	8.5	7,30 (CH_2) 2,8 (C_6H_5)	9,00	4,9	3,1	−11,5	3,0	0,9
XXIIIA	CH_3	$CH_2CH_2C_6H_5$	—	9,08	7,85	7,10	7,10	8.5	8,86	2,92 (C_6H_5)	—	2,8	—	—	—
XXIIIB	$CH_2CH_2C_6H_5$	CH_3	—	9,08	7,85	7,10	7,10	8.5	2,92 (C_6H_5)	8,88	—	2,8	—	—	—
XXIVA	CH_3	$CH{=}CHC_6H_5$	8,62	9,00	7,78	7,00	7,00	8,6	8,75	3,75 (α-H) 3,45 (β-H) 2,7 (C_6H_5)	4,6	2,7	—	—	—
XXIVB	$CH{=}CHC_6H_5$	CH_3	8,62	8,95	7,83	7,10	7,10	8,6	3,92 (α-H) 3,32 (β-H) 2,7 (C_6H_5)	8,75	4,6	2,7	—	—	—

*$^2J_{6\text{-exo, -endo}}$ and $^3J_{4\text{-endo},5} \leq 0.5$ Hz; $^4J_{2\ 6\text{-endo}} \approx 0.5$ Hz in the endo isomers of VI-XVIII.
†Abbreviations: A is the endo isomer, and B is the exo isomer.

TABLE 2. Contributions of an Aromatic Solvent [$\Delta\tau = \tau_{C_6H_6} - \tau_{CCl_4}$ (ppm)] to the Shielding of the Protons of Substituted 1,3-Diazabicyclo[3.1.0]hexanes

Compound	ΔH_5-exo	ΔH_6-endo	ΔH_1-endo	ΔH_4-exo	ΔR	ΔR′
I	0,06	0,40	0,26	0,12	−0,14	+0,06
II	0,15	0,17	0,25	0,13	−0,02	0,01
III	0,13	0,27	0,31	0,20	−0.10 (CH_2)	0,09 (CH_2)
IV	0.03	0,17	0,15	0,03	—	—
V	0,08	0,27	0,13	0,13	—	—
VIA	0,04	0,25	0,13	0,06	−0,09	+0,03
VIB	0,02	0,28	0,11	0,06	−0,08	0
VIIA	—	—	0,28	0,08	−0,11	—
VIIB	—	—	0,23	0,08	—	+0,04
VIIIA	0,36	0,50	0,64	0,42	+0,21	—
VIIIB	0,37	0,77	0,70	0,29	—	+0,59
IXA	0,17	0,27	0,40	0,20	0	—
IXB	0,20	0,47	0,48	0,15	—	+0,27
XA	0,14	0,25	0,33	0,17	−0,05	—
XB	0,15	0,39	0,41	0,12	—	+0,19
XIA	0,19	0,31	0,37	0,19	−0,01	—
XIB	0,21	0,38	0,41	0,08	—	+0,30
XIIA	0,17	0,34	0,42	0,24	−0,07	—
XIIB	0,18	0,50	0,47	0,19	—	+0,20
XIIIA	0,17	0,23	0,35	0,16	−0,11	—
XIIIB	0,19	0,46	0,41	0,09	—	+0,17
XIVA	0,06	0,15	0,28	0,14	−0,19	—
XIVB	0,09	0,36	0,35	0,07	—	+0,06
XVA	0,02	0,07	0,22	0,04	−0,20	—
XVB	0,04	0,22	0,27	−0,2	—	−0,02
XVIA	0,01	0,05	0,23	0,05	−0,33	—
XVIB	0,06	0,37	0,28	−0,03	—	−0,06
XVIIA	0,02	−0,03	0,26	0,12	−0,11	—
XVIIB	0,02	0,31	0,07	−0,13	—	+0,02
XVIIIA	0,09	0,17	0,33	0,16	−0,16	—
XVIIIB	0,14	0,41	0,28	0,11	—	0,06
XIXA	0,04	0,36	0,25	0,15	−0,09	—
XIXB	0,04	0,36	0,25	0,12	—	0,05
XXA	0,35	0,56	0,55	0,52	0,09	—
XXB	0,45	0,60	0,32	0,28	—	0,38
XXIA	0,15	0,22	0,40	0,40	−0,12	—
XXIB	0,15	0,44	0,40	0,16	—	0,09
XXIIA	0,14	0,23	0,39	0,14	−0,06	0,05 (CH_2)
XXIIB	0,14	0,35	0,37	0,13	−0,05 (CH_2)	0,11
XXIIIA	—	0,25	0,23	0,23	−0,10	—
XXIIIB	—	0,25	0,23	0,23	—	0,16
XXIVA	0,12	0,29	0,25	0,25	−0,04	−0,09 (α-H)
XXIVB	0,15	0,40	0,25	0,25	−0,26 (α-H)	0,10

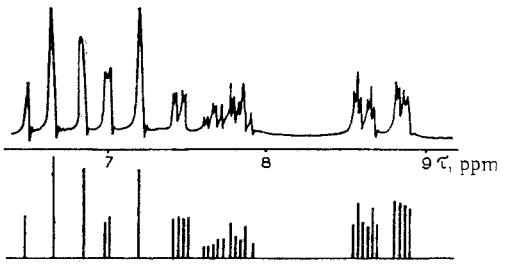

Fig. 1

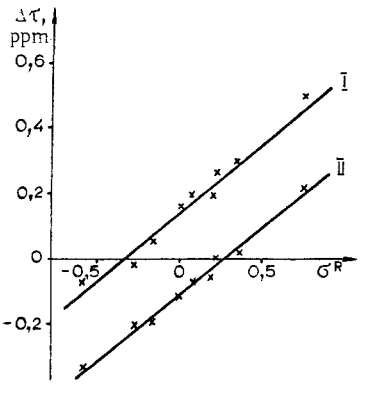

Fig. 2

Fig. 1. Experimental and theoretical PMR spectra of 1,3-diazabicyclo[3.1.0]hexane in D_2O.

Fig. 2. Relationship between $\Delta\tau = \tau_{C_6H_6} - \tau_{CCl_4}$ for the 2-H proton and the Hammett σ constants: I) exo isomer; II) endo isomer.

result is not expected, inasmuch as the boat form is extremely characteristic for bicyclic compounds of the [3.1.0] type (for example, see [6]).

The assignment of the lines of the spectra to the resonance of protons of a definite isomer (XIIIA or XIIIB) was made on the basis of an evaluation of the contributions of the anisotropy of the phenyl ring to the

TABLE 3. 2,2-Disubstituted 1,3-Diazabicyclo[3.1.0]hexanes

Compound	R	R′	mp or bp (mm), °C	n_D^{20}	d_{20}	MR_D found	MR_D calc.	Empirical formula	Found, % C	Found, % H	Found, % N	Calc., % C	Calc., % H	Calc., % N	Yield, %
IV	—$(CH_2)_4$—		67—69 (2)	1,5029	0,9577	39,05	40,63	$C_8H_{14}N_2$	70,4	9,0	20,1	70,6	8,7	20,6	85
V	—$(CH_2)_5$—		80—81	—	—	—	—	$C_9H_{16}N_2$	70,7	10,2	18,2	71,0	10,5	18,4	90
XXI	C_6H_5	CH_3	101—103 (3)	1,5530	1,036	52,26	52,54	$C_{11}H_{14}N_2$	75,2	8,7	16,4	75,9	8,0	16,1	78
XX	p-$NO_2C_6H_4$	CH_3	95—96	—	—	—	—	$C_{11}H_{13}N_3O_2$	60,2	5,8	18,8	60,3	5,9	19,2	94
XXII	$C_6H_5CH_2$	CH_3	117—119 (2)	1,5505	1,0342	57,72	57,16	$C_{12}H_{16}N_2$	74,8	8,7	16,0	75,0	9,1	15,9	76
XXIII	$C_6H_5CH_2CH_2$	CH_3	144—146 (4)	1,5390	1,0297	62,24	61,78	$C_{13}H_{18}N_2$	77,1	9,0	13,5	77,2	8,9	13,9	69
III	$C_6H_5CH_2$	$CH_2C_6H_5$	174—176 (2)	1,5850	1,0546	76,45	76,07	$C_{18}H_{20}N_2$	82,0	7,2	10,1	81,8	7,6	10,6	86
XXIV	$C_6H_5CH{=}CH$	CH_3	152—154 (2)	1,5736	—	—	—	$C_{13}H_{16}N_2$	77,8	8,0	14,1	78,0	8,0	14,0	64
XVII	$C_6H_5CH{=}CH$	H	154—156 (2)	—	1,5675	—	—	$C_{12}H_{14}N_2$	77,3	7,3	15,3	77,4	7,5	15,0	67
XVIII	2-Furyl	H	79—81	—	—	—	—	$C_8H_{10}N_2O$	64,4	6,5	18,6	64,0	6,7	18,7	90

shielding of the endo H_6 protons in both forms, in the calculation of which only the most energetically favorable conformations of the phenyl ring, exposed by means of conformational analysis of XIII by the Westheimer method,* were taken into account. The results of the calculations show that the resonance of this proton in the spectrum of the endo isomer should be observed at stronger field, whereas the resonance of this proton in the exo isomer should be observed at weaker field as compared with the unsubstituted bicyclic I molecule. Bearing this in mind and also comparing the intensities of the corresponding signals, no difficulties are encountered in the assignment of the individual lines in the spectrum to the protons of the endo and exo forms of XIII. A similar procedure was also used for the analysis of the spectra of VIII-XVIII. In the case of 2-methyl- and 2-ethyl-substituted VI and VII, as well as 2,2-disubstituted bicyclic compounds XIX-XXIV, the difference in the exo and endo forms is distinctly displayed during a study of the shifts induced by an aromatic solvent (see below). The correctness of the assignment was confirmed by a study of the dipole moments of the isomers of X: $\mu = 2.5$ D (as compared with 1.7 D calculated via a vector scheme) for the endo form of X, and $\mu = 3.8$ D (as compared with 2.8 D calculated by a vector scheme) for the exo form of X. Confirmation was also obtained by x-ray-diffraction analysis of the exo form of IX.†

A long-range SSCC between the 4-exo and 6-exo protons, which have a W-shaped orientation [7], is distinctly observed in the spectra of the investigated compounds. Somewhat unexpectedly, it was found the 2-exo proton in the endo isomers of VIII-XVIII have a long-range SSCC with the 6-endo proton but not with the 6-exo proton. The reason for this may be the effective (with respect to stereochemical considerations) σ-π conjugation between the C_2-H_{exo} bond and the p electrons of the N and C atoms of the three-membered ring, which has been discussed in the case of epoxides and cyclopropanes [8].

One's attention is drawn to the fact that the internal chemical shift between the 4-H protons in the exo isomers of VI-XVIII differs only slightly from that observed for unsubstituted bicyclic I. In addition, for the endo forms of VI-XVIII this value is almost halved. Moreover, the difference in the position of the resonance lines of the 2-H protons in the exo and endo isomers of VI-XVIII is considerably lower in magnitude and opposite in sign as compared with the difference in the shielding of the endo and exo 2-H proton in I. Inasmuch as the anisotropy of the substituent in the 2 position does not explain the observed changes in the shielding of 2-H and 4-H, the latter are probably due to the different orientation of the unshared pairs of the electrons of the N_1 and N_3 atoms in the exo and endo isomers of VI-XVIII. Calculations show that the best agreement is a achieved if it is assumed that the unshared electron pair of the N_3 atom in I and exo isomers of VI-XVIII has primarily an endo orientation and that in the endo isomers it is directed in the opposite direction, possibly because of repulsion between it and the substituent. This result is confirmed by the different complexing constants of the endo and exo isomers with tris(dipivaloylmethanato)europium, which will be the subject of a separate communication. The orientation of

*The results of the conformational analysis of XIII will be published separately.

†The results will be published later.

the N_1 and N_3 electron pairs in I is also not surprising, if one takes into account their mutual repulsion (the "rabbit-ears effect" [9]).

We also studied the effect of an aromatic solvent on the resonance of the protons in the PMR spectra of bicyclohexanes I-XXIV (Table 2). In both isomers the 6-H endo proton is more sensitive than the exo proton to the effect of benzene. This is due to the closeness of the latter to the unshared electron pair of the N_1 atom [10]. The contribution of benzene to the shielding of the 6-H endo protons for the exo isomers considerably exceeds the corresponding contribution observed for the endo isomers. The reason for this difference may consist in the greater steric hindrance to solvation inherent in the endo form. The effect of benzene on the shielding of the 2-H protons is also different: the endo proton experiences the greatest shift to strong field, while the signal of the exo proton is only slightly sensitive to the effect of the solvent. The same is valid for the signals of the methyl groups in the 2 position. We used this fact to assign the absorption signals to the endo and exo isomers of VI, VII, and XVII-XXIV.

It should be noted that the effect of the aromatic solvent on the signals of the 2-H protons weakens symbatically with the Hammett σ substituent constants of the phenyl ring as the electron-donor capacity of the substituent in VIII-XVIII increases (Fig. 2). This indicates the electrostatic nature of the complexes formed.

Using the different solubilities of the endo- and exo-2-substituted 1,3-diazabicyclo[3.1.0]hexanes, we were able to isolate the endo-2-(p-chlorophenyl) derivative containing only traces of the exo isomer. Periodic checks of this sample in the course of a month did not reveal appreciable isomerization when it was stored in the crystalline form. However, when the preparation was dissolved in CCl_4, appreciable amounts of the exo isomer were detected even after a few hours, and equilibrium is established between both forms after 24 h (endo:exo = 53:47 at 36°). It is curious that irradiation with x-ray beams (~3 nm) for several days of the equilibrium crystalline mixture of the exo and endo isomers of 2-(p-bromophenyl)-1,3-diazabicyclo[3.1.0]hexane leads to an appreciable increase in the percentage of the exo isomer. These observations graphically demonstrate the possibility of interconversions of one form of the bicyclic compounds investigated by us to the other.

EXPERIMENTAL

The PMR spectra of the compounds were obtained with a Perkin-Elmer R 12A spectrometer. The chemical shifts were measured with an accuracy of ± 0.5% from the degree of scan. The compounds were investigated in the form of 10% solutions in CCl_4 and benzene. The internal standard was tetramethylsilane. The spectrum of I was also obtained in D_2O with sodium 3-(trimethylsilyl)propanesulfonate as the internal standard. The effect of the anisotropy of the benzene ring was calculated by the method in [11]. The theoretical PMR spectra were calculated by means of the LAOCON3 program with an HP 2116C computer.

The synthesis of I, II, VI, VII, and XIX was described in [3], and the synthesis of VIII-XVI was described in [2]. Bicyclic XVIII was synthesized by the method in [2].

Bicyclohexanes III-V and XX-XXIII (Table 3). A) A 0.1-mole sample of a solution of the appropriate ketone in 50 ml of absolute alcohol was added with stirring to a solution of 7.2 g (0.1 mole) of 2-(aminomethyl)ethyleneimine in 20 ml of absolute alcohol, after which the mixture was refluxed for 2-3 h. It was then cooled, dried with calcium hydride, and filtered. The alcohol was removed from the filtrate by distillation, and the solid products were recrystallized from ether or hexane, and the liquids were vacuum distilled.

B) A 0.1-mole sample of the appropriate ketone in 50 ml of absolute benzene was added to a solution of 7.2 g (0.1 mole) of 2-(aminomethyl)ethyleneimine in 50 ml of absolute benzene, and the mixture was refluxed with a Dean–Stark trap until 0.1 mole of water had been removed by distillation. The solvent was then evaporated, and the mixture was worked up as in method A.

The details of the synthesis of XVII and XXIV will be published at a later date.

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