LITERATURE CITED

1. G. I. Migachev, A. M. Andrievskii, A. N. Poplavskii, and N. S. Dokunikhin, USSR Inventor's Certificate No. 591,473; Byull. Izobret., No. 5, 76 (1978).
2. G. I. Migachev, A. M. Andrievskii, and N. S. Dokunikhin, Zh. Org. Khim., 13, 463 (1977).
3. G. I. Migachev, L. V. Eremenko, K. M. Dyumaev, and N. S. Dokunikhin, Zh. Org. Khim., 14, 668 (1978).
4. A. M. Andrievskii, A. N. Poplavskii, and M. M. Dyumaev, USSR Inventor's Certificate No. 811,766; Byull. Izobret., No. 5, 283 (1983).
5. A. N. Kost (ed.), General Laboratory Course in Organic Chemistry [Russian translation], Mir, Moscow (1965), p. 615.

CONFORMATION OF 5,5-DISUBSTITUTED 2,2-DIMETHYL-1,3-DIOXANES

B. O. Kraiz

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It was established by PMR spectral data that in solutions of derivatives of 5-acetoxymethyl-, 5-methyl-, and 5-hydroxymethyl-2,2-dimethyl-1,3-dioxanes with nitrogen-containing substituents (2,4-disubstituted 1,3,5-triazin-6-ylamino, benzamido, and nitro groups) with an N—$C_{(5)}$ bond the 1,3-dioxane ring exists in the chair conformation with primarily an axial orientation of the nitrogen-containing substituent. Depending on the nature of the substituents attached to the $C_{(5)}$ atom, the 1,3-dioxane ring may exist either in the stable chair conformation or may undergo rapid inversion of the chair-chair type at 20°C.

It has been previously shown [1, 2] that stereoisomers of 5-(1,3,5-triazin-6-ylamino)-1,3-dioxanes exist in the chair conformation in solutions. Because of strong 1,3 interactions, 2,2-disubstituted 1,3-dioxanes may take on not only the chair conformation but also the boat conformation [3-5], as well as 1,4- and 2,5-twist forms [6]. In this connection, it was of interest to study the effect of some nitrogen-containing substituents with an N—$C_{(5)}$ bond of the 1,3-dioxane ring on its conformation in 5-methyl-, 5-acetoxymethyl-, and 5-hydroxymethyl-2,2-dimethyl-1,3-dioxanes (I-XII, Table 1). In the PMR spectra* of solutions of 5-[2,4-bis-(dimethylamino-1,3,5-triazin-6-ylamino]-2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (I) [7], 5-acetoxymethyl-5-[2,4-bis(dimethyamino)-1,3,5-triazin-6-ylamino]-2,2-dimethyl-5-(4-diethylamino-2-chloro-1,3,5-triazin-6-ylamino)-5-hydroxymethyl-1,3-dioxane (V) [7] in chloroform and d_6-acetone (Fig. 1 and Table 1) the nonequivalent axial and equatorial protons in the 4 and 6 positions of the dioxane ring have a singlet signal at 20°C. The methyl groups in the 2 position are also characterized in the spectra by one signal. Assuming that rapid inversion of the conformations of the 1,3-dioxane ring of the chair-chair type occurs in the indicated solvents at 20°C, we studied the PMR spectra of these compounds in d_6-acetone at low temperatures. Signs of splitting of the singlet signal of the methylene protons attached to $C_{(4)}$ and $C_{(6)}$ appear in the spectrum of III at −49°C, and the overall quartet of the AB system of the same protons is observed at −62°C; this is characteristic for the stable chair conformation. Splitting of the singlet signal of the methylene protons attached to $C_{(4)}$ and $C_{(6)}$ was not observed in the PMR spectra of I and V when the temperature was lowered to −90°C. However, the similarly constructed 5-[2,4-bis(aziridino)-1,3,5-triazin-6-ylamino]-2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (II) exists in the stable chair conformation at 20°C, which indicates that a rapid inversion of the conformations of the chair-chair type is actually characteristic for I and V; for dioxane derivatives I, III, and V the preferred conformation is

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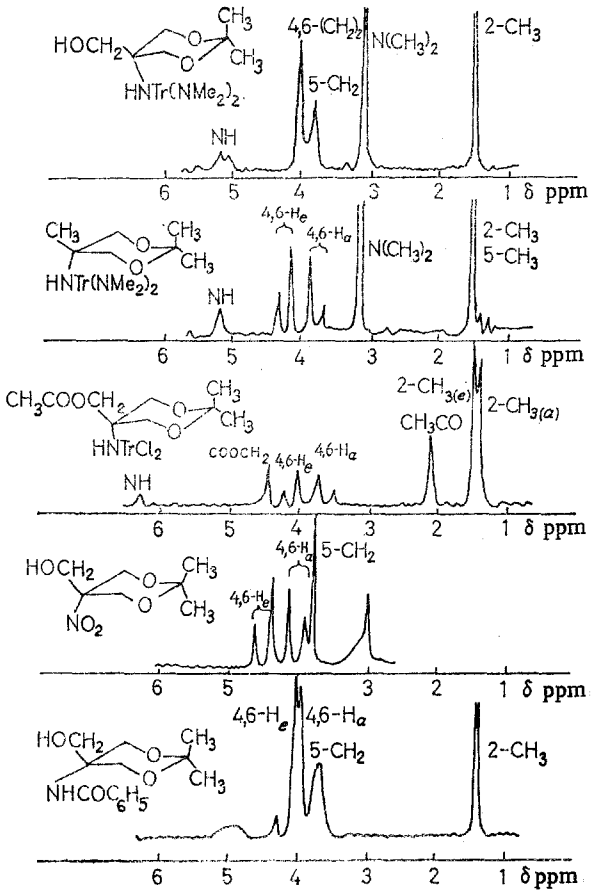
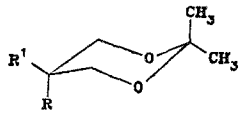


Fig. 1. PMR spectra of 5,5-disubstituted 2,2-dimethyl-1,3-dioxanes I, IV, VII, IX, and XI in $CDCl_3$, $CHCl_3$, and CH_3CN.

a chair conformation with an equatorial CH_2OR group, as evidenced by the closeness of the chemical shifts of the methylene protons of this group in the spectra of I, III, and V to the shifts of the CH_2OR group for 2-substituted 1,3-dioxanes, which have a chair conformation with an equatorial 5-CH_2OR group (XIIIa, Table 2, and the data in [1, 2]). The preferableness of this conformation corresponds to the greater size of the CH_2 group as compared with the NH group.

In the PMR spectrum of a solution of 5-[2,4-bis(dimethylamino)-1,3,5-triazin-6-ylamino]-2,2,5-trimethyl-1,3-dioxane (IV) in chloroform (Fig. 1 and Table 1) one observes an overall quartet of two methylene groups in the 4 and 6 positions with a difference ($\Delta\delta$) in the chemical shifts of the axial and equatorial protons of 0.46 ppm, which indicates the existence of a stable chair conformation. At the same time, the methyl groups in the 2 and 5 positions of the dioxane ring have an overall narrow signal. The magnitude of the shift of the methyl group in the 5 position (δ 1.40 ppm) corresponds to its equatorial orientation, as in the case of 5-methyl-5-nitro-2-phenyl-1,3-dioxane (XIVa) with an equatorial methyl group (δ 1.27 ppm, Table 2) in the chair conformation or as in the case of 5-nitro-2,2,5-trimethyl-1,3-dioxane (X) (δ 1.40 ppm for the 5-CH_3 group), the conformation of which was previously proved [8] by the method of dipole moments. In the case of stereoisomer XIVb δ_H of the 5-CH_3 group proved to be 1.85 ppm; the methylene protons attached to $C_{(4)}$ and $C_{(6)}$ are characterized in the spectrum by one signal. In the case of stereoisomer XIVa, which exists in the stable chair conformation, the $\Delta\delta_{ae}$ value of the methylene protons is 1.07 ppm. At the same time, in the case of 2,2-dimethyl-1,3-dioxane X the $\Delta\delta_{ae}$ value of the methylene protons is 0.53 ppm in acetonitrile and 0.67 ppm in chloroform. This shows that one cannot form a judgment regarding the preferred orientation of the substituent attached to $C_{(5)}$ in the chair conformation of the 1,3-dioxane ring in 2,2-dimethyl-1,3-dioxanes from the magnitude of the $\Delta\delta_{ae}$ value of the methylene protons attached to $C_{(4)}$ and $C_{(6)}$. Of greater significance in this case is the chemical shift of the protons of this substituent. A similar situation is observed when one compares the PMR spectra of 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane (IX) [9] and 5-nitro-5-hydroxymethyl-2-phenyl-1,3-dioxane isomers (XIIIa,b). These compounds exist in the stable chair conformation, according to the signs indicated above. The shift of the hydroxymethyl group in IX virtually coincides with that for XIIIa with an equatorial hydroxymethyl

TABLE 1. PMR Spectra of 5,5-Disubstituted 2,2-Dimethyl-1,3-dioxanes

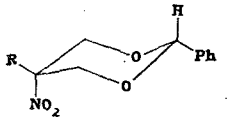


Compound	R	R'	Solvent	δ, ppm						J_{AB}, Hz
				2-Me		4-H, 6-H		R'		
				a	*e*	*a*	*e*	*a*	*e*	
I	NHTr(NMe$_2$)$_2$*	CH_2OH	$CDCl_3$	1,38		3,86		3,73		—
			d_7-DMF	1,35		4,03		3,89		—
II	NHTr[N(CH$_2$)$_2$]$_2$	CH_2OH	d_6-DMSO	1,33	1,50	3,75	4,15	3,66		12
III	NHTr(NMe$_2$)$_2$	CH_2OAc	$CDCl_3$	1,36		4,03		3,60		—
			$(CD_3)_2CO$	1,35	1,40	4,09		4,64		—
IV	NHTr(NMe$_2$)$_2$	CH_3	$CHCl_3$	1,40		3,69	4,15	1,40		12
			$(CD_3)_2CO$	1,37	1,39	3,76	4,14	1,43		10,8
V	NHTrCl, NEt$_2$	CH_2OH	$CHCl_3$	1,38		3,88		3,80		—
VI	NHTrCl$_2$	CH_2OH	CH_3CN	—		3,88	4,10	3,85		13
VII	NHTrCl$_2$	CH_2OAc	$CHCl_3$	1,40		3,83	4,14	4,45		12
VIII	NHTrCl$_2$	CH_3	$CHCl_3$	1,37	1,40	3,69	3,89	1,32		12
IX	NO_2	CH_2OH	CH_3CN	—		3,94	4,37	3,73		13,8
			$(CD_3)_2CO$	1,33	1,43	4,11	4,51	3,93		10,8
X	NO_2	CH_3	CH_3CN	1,30	1,47	4,00	4,53	1,40		13,4
			$CHCl_3$	1,27	1,35	3,77	4,44	1,37		12,5
XI	$NHCOC_6H_5$	CH_2OH	$CHCl_3$	1,39		3,83	4,10	3,82		12
XII	$NHCOC_6H_5$	CH_2OAc	$(CD_3)_2CO$	1,43	1,46	4,07	4,31	4,60		11,2

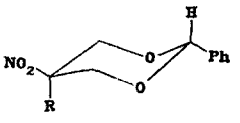
*The 1,3,5-triazinyl group is designated by Tr.

TABLE 2. PMR Spectra and Structures of the Separated Stereoisomers of 5-Hydroxymethyl- and 5-Methyl-5-nitro-2-phenyl-1,3-dioxanes XIIIa,b and XIVa,b

Structure a



Structure b



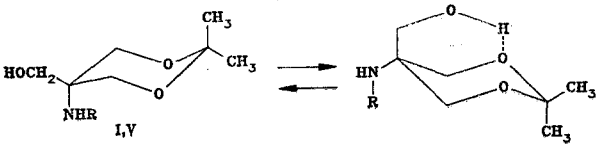
Compound	Solvent	δ, ppm					$\Delta\delta_{ae}$	J_{ae}, Hz
		2-H	4-H, 6-H		R			
			a	*e*	*a*	*e*		
XIII	CH_3CN	5,59	4,10	4,88	—	3,74	0,78	12
XIII	CH_3CN	5,49	4,19	4,50	4,22	—	0,31	10,5
XIV	$CHCl_3$	5,40	3,80	4,87	—	1,27	1,07	12
XIV	$CHCl_3$	5,40	4,23		1,85	—	0	0

group attached to $C_{(5)}$ (Tables 1 and 2) and constitutes evidence for the primarily equatorial orientation of the hydroxymethyl group in IX. At the same time, the $\Delta\delta_{ae}$ value of the methylene protons attached to $C_{(4)}$ and $C_{(6)}$ in 2,2-dimethyl-1,3-dioxane IX (0.43 ppm) is closer to the $\Delta\delta_{ae}$ value of the same protons in isomer XIIIb (0.31 ppm) than in isomer XIIIa (0.78 ppm). According to the PMR spectral data, just as for II, IV, IX, and X, a long-lived (on the NMR time scale) chair conformation is realized for 5-(2,4-dichloro-1,3,5-triazin-6-ylamino)-2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (VI) [7] in acetonitrile, 5-acetoxymethyl-5-(2,4-dichloro-1,3,5-triazin-6-ylamino)-2,2-dimethyl-1,3-dioxane (VII) [7] in chloroform, 5-(2,4-dichloro-1,3,5-triazin-6-ylamino)-2,2,5-trimethyl-1,3-dioxane (VIII) [10] in chloroform, 5-benzamido-2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (XI) in chloroform, and 5-acetoxymethyl-5-benzamido-2,2-dimethyl-1,3-dioxane (XII) in d_6-acetone (Fig. 1 and Table 1). The shifts of

the protons of the CH_2OH, CH_2OAc, and CH_3 groups attached to the $C_{(5)}$ atom of the 1,3-dioxane ring in VI-VIII, XI, and XII show that these groups occupy primarily an equatorial orientation, as in the case of dioxane derivatives I-V, IX, and X.

A comparison of the conformations of the dioxane rings of all of the examined compounds shows that an axial orientation is the most favorable for the indicated substituents with an N—$C_{(5)}$ bond; in the majority of cases one observes the stable chair conformation, despite the strong 1,3 interactions of the axial hydrogen atoms attached to $C_{(4)}$ and $C_{(6)}$ with the methyl group attached to $C_{(2)}$ of the 1,3-dioxane ring.

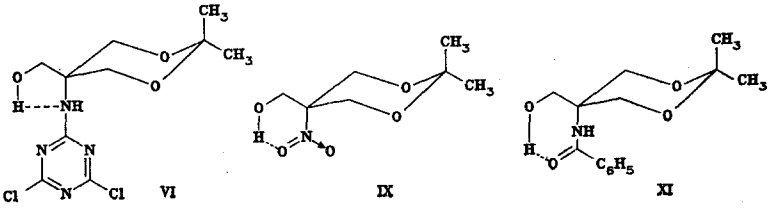
Rapid inversion of the chair conformation is observed in the PMR spectra only for I and III, in which a 2,4-bis(dimethylamino)-1,3,5-triazin-6-ylamino group and CH_2OAc groups, respectively, are located in the 5 position of the dioxane ring, and for V with 4-diethylamino-2-chloro-1,3,5-triazin-6-ylamino and hydroxymethyl groups. However, replacement of the hydroxymethyl group by a methyl group (IV) or electron-donor 2,4-bis(dimethylamino)-1,3,5-triazin-6-ylamino and 4-diethylamino-2-chloro-1,3,5-triazin-6-yl amino groups by electron-acceptor 2,4-dichloro-1,3,5-triazin-6-ylamino, nitro, and benzamido groups (VI, IX, and XI) leads to the stable chair conformation. The hydroxymethyl group in I and V evidently has the ability to form an intramolecular hydrogen bond with the oxygen atoms of the 1,3-dioxane ring, the proton-acceptor ability of which is intensified under the influence of the electron-donor substituents indicated above. The possibility of an intramolecular hydrogen bond of the CH_2OH group with the oxygen atoms of the dioxane ring was demonstrated in a study of the configurations and conformations of 2-aryl-5-[2,4-bis(dimethylamino)-1,3,5-triazin-6-ylamino]-5-hydroxymethyl-1,3-dioxanes [1]. The isomers with an axial hydroxymethyl group exist in solution in chloroform in a rigid chair conformation, whereas rapid inversion of the chair conformation is observed in the PMR spectra for such isomers in the proton-acceptor solvents d_7-DMF and d_6-acetone; this indicates disruption of the intramolecular hydrogen bond that stabilizes the rigid chair conformation in a slightly polar solvent.



I,V

The existence of an intramolecular hydrogen bond also in VI and IX with electron-acceptor substituents was previously detected by means of IR spectroscopy [9-11] and was also observed in the present research for benzamido-substituted XI. In the IR spectrum of the latter in chloroform one observes two absorption bands at 3200-3700 cm^{-1}. One of them is related to the absorption of an NH group, and the second broader band (3310-3360 cm^{-1}) is related to the OH group, since it vanishes in the spectrum of XII obtained by acetylation of hydroxymethyl derivative XI. Since an absorption band of a free OH group at 3600-3700 cm^{-1} does not appear in the spectrum in the case of dilution of a sample of XI in chloroform, the band at 3310-3360 cm^{-1} should be ascribed to the absorption of an intramolecularly bonded OH group.

Since VI, IX, and XI in solutions in chloroform and acetonitrile exist primarily in the form of a conformer with an equatorial hydroxymethyl group, it may be assumed that the electron-acceptor substituent, by decreasing the electron density on the oxygen atoms of the 1,3-dioxane ring, itself forms an intramolecular hydrogen bond with the hydroxymethyl group:



VI IX XI

EXPERIMENTAL

The PMR spectra of solutions of the substances in deuterochloroform, chloroform, acetonitrile, d_6-acetone, and d_7-dimethylformamide were recorded at 20°C with a C-60 HL spectrometer; the spectra of solutions of I, III, and V in d_6-acetone were recorded at +10°C to −90°C. The IR spectra were obtained with a UR-10 spectrometer.

5-Acetoxymethyl-5-[2,4-bis(dimethylamino)-1,3,5-triazin-6-ylamino]-2,2-dimethyl-1,3-dioxane (III). A 0.15-ml (1.6 mmole) sample of acetic anhydride was added to a solution of 0.5 g (1.5 mmole) of 5-hydroxymethyl-substituted 1,3-dioxane I in 1 ml of anhydrous pyridine, and the mixture was allowed to stand overnight at 20°C. It was then poured over ice, and the resulting precipitate was removed by filtration to give 0.49 g (86%) of III with mp 107-108.5 °C (from aqueous methanol). Found, %: N 22.7. $C_{16}H_{28}N_6O_4$. Calculated, %: N 22.8.

2,2-Dimethyl-5-(4-diethylamino-2-chloro-1,3,5-triazin-6-ylamino)-5-hydroxymethyl-1,3-dioxane (V). A 12-mg sample of p-toluenesulfonic acid was added to a solution of 1 g (3.3 mmole) of 2-(4-diethylamino-2-chloro-1,3,5-triazin-6-ylamino)-1,3-propanediol, and the mixture was maintained at 20°C for 3 days. The acetone was removed by distillation, the residue was dissolved in benzene, and the benzene solution was washed with aqueous $NaHCO_3$ solution and water. The benzene was removed *in vacuo*, and the residue was treated with water. The next day the solidified product was removed by filtration to give 0.95 g (84%) of V with mp 98-100°C (from hexane). Found, %: Cl 10.2, N 20.4. $C_{14}H_{24}ClN_5O_3$. Calculated: Cl 10.3, N 20.3.

5-Benzamido-2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (XI). A 2.8-g (20 mmole) sample of benzoyl chloride was added at 5°C to a suspension of 4.84 g (40 mmole) of thoroughly ground 2-amino-2-hydroxymethyl-1,3-propanediol in 120 ml of anhydrous acetone, and the mixture was stirred at 5°C for 1 h and at 20°C for 4 h. It was then heated to 40-50°C, and the precipitated hydrochloride of the starting amine was removed by filtration and washed with 20 ml of hot acetone. The combined filtrate was evaporated *in vacuo*, hexane was added to the solid residue, and the precipitate was removed by filtration to give 4.14 g (92%) of 2-benzamido-2-hydroxymethyl-1,3-propanediol with mp 130-131°C (from ethyl acetate). Found, %: C 59.0, H 7.0, N 6.3. $C_{11}H_{15}NO_4$. Calculated, %: C 58.5, H 6.7, N 6.2. A mixture of 2.25 g (10 mmole) sample of 2-benzamido-2-hydroxymethyl-1,3-orppanediol, 1.98 g (15 mmole) of 2,2-diethoxypropane, and 19 mg of p-toluenesulfonic acid in 20 ml of anhydrous benzene was refluxed on a water bath for 1 h, after which the solution was washed with aqueous $NaHCO_3$ solution, dried with sodium sulfate, and evaporated *in vacuo*. The oily residue was treated with 15 ml of hexane, and the crystallized product was removed by filtration to give 2.1 g (79%) of XI with mp 103-105°C (from CCl_4). Found, %: C 63.2, H 7.3, N 5.4. $C_{14}H_{19}NO_4$. Calculated, %: C 63.4, H 7.2, N 5.3.

5-Acetoxymethyl-5-benzamido-2,2-dimethyl-1,3-dioxane (XII). A 0.65-g (2.4 mmole) sample of XI and 0.26 ml (3.6 mmole) of acetyl chloride were refluxed in 5 ml of CCl_4 for 1 h, after which the mixture was evaporated *in vacuo*, the residue was treated with aqueous $NaHCO_3$ solution, and the precipitated solid product was removed by filtration to give 0.5 g (87%) of XII with mp 96-98°C (from aqueous ethanol). Found, %: C 62.7, H 7.0, N 4.7. $C_{16}H_{21}NO_5$. Calculated, %: C 62.5, H 6.8, N 4.6.

Stereoisomers of 5-Nitro-5-hydroxymethyl-2-phenyl-1,3-dioxane (XIIIa,b). A 5.75-g (38 mmole) sample of 2-nitro-2-hydroxymethyl-1,3-porpanediol, 4.14 g (39 mmole) of freshly distilled benzaldehyde, and 10 mg of p-toluenesulfonate were heated in 40 ml of benzene on a water bath for 3 h until water liberation in a Dean–Stark trap ceased. After removal of most of the benzene by distillation, the residue was treated with 50 ml of hexane, and the precipitate was removed by filtration, washed with aqueous $NaHCO_3$ solution and water, and air-dried at 60°C to give 7.8 g (86%) of a mixture of isomers XIIIa,b, which was separated by fractional crystallization from benzene and precipitation by means of cyclohexane from a concentrated benzene solution. The purity of the isolated isomers was monitored by thin-layer chromatography on a Silufol UV-254 plate in ethyl acetate–chloroform (1:4). Isomer XIIIa had mp 125°C (from benzene) and R_f 0.22. Found, %: N 5.9. $C_{11}H_{13}NO_5$. Calculated, %: N 5.8. Isomer XIIIb had bp 85.5-88°C (from benzene–cyclohexane) and R_f 0.8. Found, %: N 6.0. $C_{11}H_{13}NO_5$. Calculated, %: N 5.8.

Stereoisomers of 5-Methyl-5-nitro-2-phenyl-1,3-dioxane (XIVa,b) [12]. The purity of the isolated isomers was monitored by TLC on a Silufol UV-254 plate in chloroform. Isomer XIVa had mp 116°C and R_f 0.66. Isomer XIVb had mp 78°C and R_f 0.82.

LITERATURE CITED

1. A. L. Remizov, B. O. Kraiz, A. I. Kol'tsov, and V. I. Alekseev, Zh. Obshch. Khim., 42, 1799 (1977).
2. B. O. Kraiz and A. L. Remizov, Khim.-farm. Zh., No. 1, 45 (1981).
3. L. K. Yuldasheva and R. P. Arshinova, Teor. Eksp. Khim., 3, 641 (1967).

4. A. V. Bogat-skii, Yu. Yu. Samitov, and Z. D. Bogat-skaya, Zh. Org, Khim., 5, 2230 (1969).
5. Yu. Yu. Samitov, G. I. Goryashin, A. V. Bogat-skii, and O. S. Stepanova, Khim. Geterotsikl. Soedin., No. 5, 614 (1968).
6. M. Anteunis, D. Tavernier, and F. Borremants, Heterocycles, 4, 293 (1976).
7. A. L. Remizov, B. O. Kraiz, and A. S. Petrov, Zh. Obshch. Khim., 40, 1616 (1970).
8. T. Urbanski, Zh. Vsesoyuzn. Khim. Obshchestva, 7, 396 (1962).
9. S. Malinowski and T. Urbanski, Roczn. Chem., 25, 183 (1951).
10. B. O. Kraiz and A. L. Remizov, Zh. Org. Khim., 15, 1282 (1979).
11. T. Urbanski, Roczn. Chem., 31, 37 (1957).
12. M. Senkus, J. Am. Chem. Soc., 65, 1656 (1943).

OXIDATIVE CYCLIZATION OF HALOBENZOPHENONE OXIMES TO 4,2'-IODONIA-3-PHENYL-1,2-BENZISOXAZOLE SALTS

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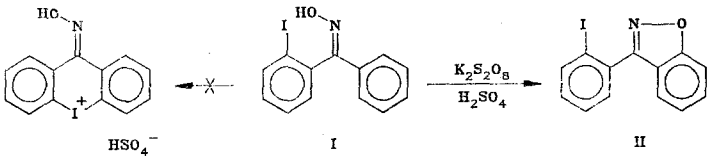
UDC 547.786.3'631.6

It is shown that the syn oximes of o-iodo- and o-, m-, and p-bromobenzophenones, under the influence of $K_2S_2O_8$ in concentrated H_2SO_4, form the corresponding 3-aryl-1,2-benzisoxazoles as a result of oxidative cyclization. 3-(2-Iodophenyl)-1,2-benzisoxazole is oxidized by peracetic acid to the iodoso derivative which, upon heating in concentrated H_2SO_4, undergoes cyclization to the 4,2'-iodonia-3-phenyl-1,2-benzisoxazole cation. The iodide, bromide, and tetrafluoroborate of this cation were isolated.

It is known that oximes of ketones are key compounds in the synthesis of a number of heterocycles, including isoxazoles and 1,2-benzisoxazoles [1]. Recently a great deal of attention has been directed to the oxidation of oximes and, chiefly, oxidative deoximation [2-4]. Several examples of the oxidative cyclization of the oximes of some not completely trivial ketones have also been described. Thus, oximes of ketones that contain a hydroxyphenyl group in the α position, under the influence of brominating agents [5], Mn^{3+} salts [6], or $Tl(NO_3)_3$ [7], give spiroisoxazolines, whereas the isomeric oximes of 2-arylidene-3-oxoquinuclidines, under the influence of Ag_2O, undergo cyclization to give five- or seven-membered heterocycles, depending on the configuration [8].

In the present paper we report a new oxidative cyclization reaction in which halobenzophenone oximes participate and describe salts of an iodonium cation that is a new heterocyclic system made up of four fused rings and is obtained as a result of double oxidative cyclization of 2-iodobenzophenone oxime.

We have previously synthesized 10-oxodibenz[b,e]iodinium salts and showed that they do not form an oxime at the carbonyl group [9]. In order to study the Beckmann rearrangement in a series of cyclic iodonium compounds we attempted to obtain 10-oximinodibenz[b,e]iodinium salts by alternative synthesis, viz., by oxidative cyclization of 2-iodobenzophenone syn-oxime (I). However, upon treatment of the latter with $K_2S_2O_8$ in concentrated H_2SO_4 cyclization pro-



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