SYNTHESIS OF NITRO-SUBSTITUTED DIOXOTETRAHYDRODIOXAPYRENES AND 6H-DIBENZO[b,d]PYRAN-6-ONE

A. M. Andrievskii, A. N. Poplavskii, L. V. Eremenko,
N. A. Andronova, and K. M. Dyumaev

UDC 547.812.5'814:
542.958.1.07

Methods for the synthesis of tri- and tetranitro-substituted 5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrenes, 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrenes, and 6H-dibenzo[b,d]pyran-6-one were developed in a search for effective sensitizers for electrophotographic layers based on carbazole-containing polymers. The possibility of the production of nitro compounds that contain three vicinal nitro groups was demonstrated. Under severe nitration conditions 2,4,8-trinitro-6H-dibenzo[b,d]pyran-6-one is cleaved to give 2-hydroxy-2'-carboxy-3,5,4'-trinitrobiphenyl, which is resistant to cyclization to give the starting compound, evidently because of the existence of an intramolecular hydrogen bond between the hydroxy group and the nitro group.

In developing our studies involving the search for new effective sensitizers for electrophotography we investigated methods for the synthesis of nitro-substituted 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (I), 5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (II) and 6H-dibenzo[b,d]pyran-6-one (III). Compound I was obtained by sublimation of the dipotassium salt of 6,6'-dinitro-2,2'-dicarboxybiphenyl [1], and II was obtained by reduction of 2,7-dinitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (IV) with hydrogen on a Raney nickel catalyst to give 2,7-diamino-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (V), diazotization of the latter, and replacement of the diazo groups by treatment with sodium hydrophosphite.

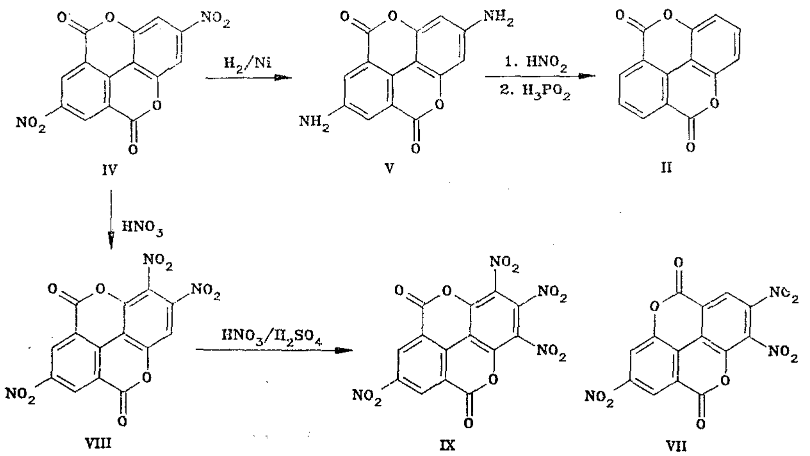
In our investigation of the nitration of dioxapyrene I we established that complex difficult-to-separate mixtures of nitro products are formed in both nitric acid and in a nitrating mixture. Compound II is difficult to obtain. We were able to develop a method for the synthesis of polynitro-substituted dioxapyrenes by using as the starting compounds for the nitration 2,7-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (VI) and IV, which were previously obtained by intramolecular nucleophilic substitution by heating, respectively, 4,4',6,6'-tetranitro-2,2'-dicarboxybiphenyl [2] and 2',4,4',6'-tetranitro-2,6-dicarboxybiphenyl [3] in strong proton-acceptor solvents. In the case of treatment of VI with a nitrating mixture we observed the formation of a mixture of nitro-substituted compounds, from which we isolated 2,3,7-trinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (VII). In the nitration of dinitrodioxapyrene IV with nitrous acid (sp. gr. 1.51) at 80°C we obtained 1,2,7-trinitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (VIII) in 89% yield. The two oxygen atoms of heterocycle IV activate the 1 and 3 positions to such an extent that vicinal trinitro compound IX can be obtained. Thus the nitration of IV or VIII in a mixture of nitric and sulfuric acids leads to the formation of 1,2,3,7-tetranitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (IX) in 90% yield.

The structures of nitro compounds VII-IX were established on the basis of the PMR spectra. Compound IV contains two pairs of equivalent protons — in the 1 and 3 positions (arbitrarily designed the α protons) and in the 6 and 8 positions (the β protons) — which is confirmed by the PMR spectrum, which contains two narrow singlet signals of identical intensity at 8.43 and 9.30 ppm. The first of these signals corresponds to the two α protons, and the second corresponds to the β protons. The spectrum of trinitropyranone VIII contains two singlet signals at 9.26 and 8.20 ppm with an integral intensity ratio of 2:1. By comparing this spectrum with the positions of the signals in the spectrum of IV, we arrive at the conclusion that replacement in one of the α protons to give a 1,2,7-substituted compound (VIII) occurred during nitra-

---

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 463-467, April, 1985. Original article submitted August 8, 1983; revision submitted September 24, 1984.

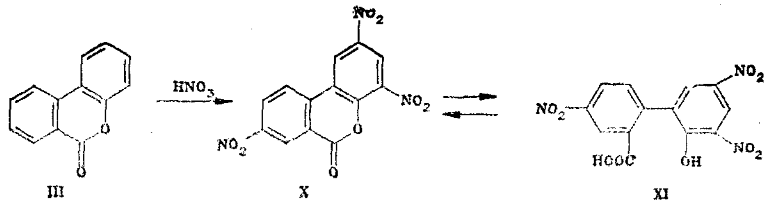
0009-3122/85/2104-0383$09.50



tion. The introduction of a fourth substituent also takes place at the site of the greatest electron density (the 3 position). The two β protons of tetranitropyranone IX are magnetically equivalent. In the PMR spectrum they are represented by one singlet signal at 9.30 ppm. With respect to the chemical shift this coincides with the position of the signals of the β protons of IV and VIII.

The spectrum of dinitropyranone VI is represented by one singlet signal at 8.9 ppm from two pairs of protons: in the 3 and 8 and 1 and 6 positions. According to quantum-chemical calculations of this compound, made by B. E. Zaitsev, the electron density on the $C_{(1)}$ and $C_{(6)}$ carbon atoms is lower by a factor of 20 than that on the $C_{(3)}$ and $C_{(8)}$ atoms. These data constitute the basis for the interpretation of the spectrum of VII. The spectrum contains a singlet signal from the proton in the 1 position at 8.60 ppm. The protons in the 6 and 8 positions give an AB system with a spectrum at 8.70 ppm in the form of two doublets with spin-spin coupling constant (SSCC) J = 2.5 Hz. The set of chemical shifts, SSCC, and signal integral intensity ratios correspond to the structure of VII.

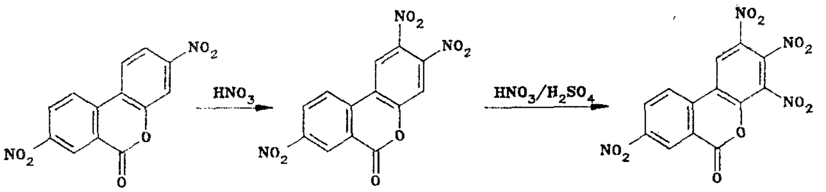
2,4,8-Trinitro-6H-dibenzo[b,d]pyran-6-one (X) is formed in 90-92% yield when III is refluxed in fuming nitric acid or treated in a nitrating mixture at room temperature. 2-Hydroxy-2'-carboxy-3,5,4'-trinitrobiphenyl (XI) begins to accumulate in the nitrating mixture when the temperature is raised. Hydroxy acid XI is quite resistant to cyclization to X; this can be explained by the existence of an intramolecular hydrogen bond between the adjacent hydroxy and nitro groups. Cyclization to give lactone X occurs when XI is treated with hydrochloric acid. The same substance was also obtained when acid XI was heated in acetic acid. A salt of hydroxy acid XI is readily formed by the action of an aqueous solution of alkali on X.



The position of the nitro groups in X was proved on the basis of the PMR spectrum. A doublet signal at 9.0 ppm from the proton in the 3 position (J = 2.5 Hz) is present at weakest field. A group of signals from protons in the 1, 7, 9, and 10 positions with SSCC of 2.5 Hz and 7.5 Hz is located at 8.23-8.60 ppm.

The nitration of 3,8-dinitro-6H-dibenzo[b,d]pyran-6-one (XII) with nitric acid gives 2,3,8-trinitro-6H-dibenzo[b,d]pyran-6-one (XIII); a compound containing three vicinal nitro groups, viz., 2,3,4,8-tetranitro-6H-dibenzo[b,d]pyran-6-one (XIV), was obtained by treatment with the nitrating mixture. The structures of XIII and XIV were proved on the basis of an x-ray diffraction study carried out by coworkers of the L. Ya. Karpov Physicochemical Scientific-Research Institute, E. G. Popova, L. A. Chetkina, and V. K. Bel'skii.

Compounds IV, VI-X, and XII were tested as electron-acceptors in compositions with poly-(N-epoxypropylcarbazole) (PEPC) under electrophotographic conditions. The best results were



XII XIII XIV

obtained for VII [exposure half life of the initial potential (H) 340 lux-sec] and X (H = 390 lux-sec); these values are somewhat inferior to the data for the composition based on PEPC and 2,4,8,10-tetranitro-6(5H)-phenanthridinone (H = 187 lux-sec) [4].

EXPERIMENTAL

The IR spectra of KCl pellets of the compounds were recorded with a Perkin-Elmer 580 spectrometer. The PMR spectra of solutions in deuterated DMSO and acetone were recorded at 25°C with a Tesla BS-467 spectrometer (60 MHz) with the same solvents as the internal standards. The purity of the products was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates.

2,7-Diamino-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (V). A 0.33-g (1 mmole) sample of IV was dissolved in 50 ml of dimethylformamide (DMF), 5 g of Raney nickel prepared by the method in [5] was added, and the compound was reduced with hydrogen at 80°C and 50 atm. After 15 min, the catalyst was removed by filtration and washed with hot DMF. The filtrate was cooled with water and poured into 150 ml of water. The resulting dark-red precipitate was removed by filtration, washed with water, and dried to give 0.19 g (72%) of V. Sublimation at 10^{-3} mm and 300°C gave V in the form of a red powder with mp 370°C, R$_f$ 0.35 [chloroform—acetic acid (9:1)], and yellow luminescence under UV irradiation. IR spectrum: 3475, 3375, 3240, 1730 (shoulder), 1715, 1620, 1490, 1375, 1175, 1090, 1030, and 930 cm^{-1}. Found, %: C 63.0, H 3.2, N 10.2. $C_{14}H_8N_2O_4$. Calculated, %: C 62.7, H 3.0, N 10.4.

5,9-Dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (II). A 0.2-g (0.75 mmole) sample of 2,7-diaminodioxapyrene V, 2.5 ml (25 mmole) of concentrated HCl, and 8 ml of water was heated on a boiling-water bath for 30 min, after which it was cooled to 0-5°C, and 0.36 ml (1.6 mmole) of a 30% solution of sodium nitrite was added in the course of 15 min. The mixture was stirred for 30 min, and a solution of 3.8 g (57.5 mmole) of sodium hypophosphite in 4.5 ml (25 mmole) of hydrochloric acid and 0.01 g (0.06 mmole) of copper sulfate were added. The mixture was stirred for 1 h and then allowed to stand overnight in the dark. The light-brown precipitate was removed by filtration, washed with water, and dried to give 0.15 g (84%) of II. Sublimation at 10^{-1} mm and 250°C gave II in the form of a colorless powder with mp 327-327.5°C, R$_f$ 0.75 [benzene—acetone (5:1)], and blue luminescence under UV irradiation. IR spectrum: 3400, 1745, 1630, 1490, 1450, 1340, 1300, 1270, 1235, 1225, 1100, 1075, 1045, and 1010 cm^{-1}. Found, %: C 70.7, H 2.6. $C_{14}H_6O_4$. Calculated, %: C 70.6, H 2.5.

2,3,7-Trinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (VII). A 1-g (3 mmole) sample of VI was added to a nitrating mixture from 3 ml (72 mmole) of nitric acid (sp. gr. 1.51) and 15 ml of sulfuric acid (sp. gr. 1.84), and the mixture was heated with stirring at 120°C for 5 h. It was then cooled, the precipitate (0.22 g) was removed by filtation, and the filtrate was poured over 100 g of ice. The resulting pink precipitate was removed by filtration, washed with water, and dried to give 0.78 g of a mixture of nitro-substituted compounds, which was crystallized from toluene with the addition of activated charcoal to give 0.6 g (53%) of light-yellow VII with mp 264-265°C and R$_f$ 0.43 [chloroform—acetic acid (10:1)] and 0.42 [dioxane—25% ammonium hydroxide (5:1)]. IR spectrum: 3400, 3090, 1765, 1615, 1575, 1545, 1440, 1410, 1360, 1310, 1205, 1170, 1125, and 1080 cm^{-1}. PMR spectrum (d$_6$-acetone): 8.60 (1H, s, 1-H) and 8.70 ppm (2H, d, $J_{6,8}$ = 2.5 Hz, 6,8-H$_2$). Found, %: C 45.2, H 1.0, N 11.2. $C_{14}H_3N_3O_{10}$. Calculated, %: C 45.0, H 0.8, N 11.3.

1,2,7-Trinitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (VIII). A 2.5-g (7.6 mmole) sample of 2,7-dinitrodioxapyrene IV was dissolved in 25 ml of nitric acid (sp. gr. 1.51), after which the mixture was stirred at 78-80°C for 30 min, cooled, and poured over 100 g of ice. The precipitate was removed by filtration, washed with water, and dried to give 2.54 g (89%) of VIII in the form of light-yellow crystals from toluene with mp 241-242°C and R$_f$ 0.48 [chloroform—acetic acid (9:1)] and 0.36 [dioxane—25% ammonium hydroxide (4:1)]. IR spectrum: 3420, 3100, 1805, 1775, 1645, 1560, 1360, 1275, 1145, 1070, 1055, 835, 815, and

730 cm^{-1}. PMR spectrum: 9.26 (2H, s, 6,8-H_2), 8.20 (s, 3-H) (d_6-acetone), 9.40 (2H, s, 6,8-H_2), 8.50 ppm (1H, s, 3-H), (d_6-DMSO). Found, %: C 45.2, H 0.8, N 11.3. $C_{14}H_3N_3O_{10}$. Calculated, %: C 45.1, H 0.8, N 11.3.

1,2,3,7-Tetranitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-dioxapyrene (IX). A 1-g (3 mmole) sample of 2,7-dinitrodioxapyrene IV was added to a nitrating mixture from 5 ml (120 mmole) of nitric acid (sp. gr. 1.51) and 25 ml of sulfuric acid (sp. gr. 1.84), after which the mixture was stirred at 120°C for 30 min, cooled, and poured over 100 g of ice. The precipitate was removed by filtration, washed with water, and dried to give 1.13 g (91%) of IX in the form of light-yellow crystals from toluene with mp 327-328°C (dec.) and R_f 0.46 [dioxane—25% ammonium hydroxide (4:1)]. IR spectrum: 3420, 3100, 1785, 1640, 1625, 1575, 1560, 1500, 1470, 1355, 1265, 1150, 1085, 1035, 855, 820, 805, 795, 735, and 715 cm^{-1}. PMR spectrum (d_6-acetone): 9.30 ppm (s, 6,8-H_2). Found, %: C 40.3, H 0.6, N 13.2. $C_{14}H_2N_4O_{12}$. Calculated, %: C 40.2, H 0.5, N 13.4.

2,3,8-Trinitro-6H-dibenzo[b,d]pyran-6-one (XIII). A 4.39-g (15 mmole) sample of dinitro compound XII was added to 50 ml of nitric acid (sp. gr. 1.51), after which the mixture was stirred at 80°C for 2 h, cooled to room temperature,and poured over ice. The precipitate was removed by filtration, washed with water, and dried to give 3.76 g (76%) of XIII in the form of yellow needles from acetic acid with mp 237.5-238.5°C (dec.) and R_f 0.22 (benzene). IR spectrum: 3450, 3100, 3075, 1775, 1630, 1560, 1540, 1490, 1360, 1280, 1255, 1210, 1110, 990, 950, 860, 845, 800, and 720 cm^{-1}. Found, %: V 47.2, H 1.5, N 12.55. $C_{13}H_5N_3O_8$. Calculated, %: C 47.1, H 1.5, N 12.7.

2,3,4,8-Tetrahydro-6H-dibenzo[b,d]pyran-6-one (XIV). An 8.58-g (30 mmole) sample of dinitro compound XII was added to a mixture of 13 ml of nitric acid (sp. gr. 1.51) and 98 ml of sulfuric acid (sp. gr. 1.84), and the mixture was stirred at 160°C for 2 h. The product was isolated as in the preceding experiment, as a result of which 8.91 g of a mixture of nitro compounds XIII and XIV was obtained. A 1-g sample of the mixture of XIII and XIV was dissolved in 80 ml of benzene—acetone (1:7) and chromatographed with a column (40 × 600) packed with Silica Gel 100/160 μm. From the first fraction, after evaporation of the eluent and recrystallization from acetic acid, we isolated 0.14 g (13%) of XIII, which was identical to the sample obtained from the preceding experiment. From the second fraction we isolated 0.82 g (64%) of XIV in the form of yellow needles from acetic acid with mp 262-263°C (dec.) and R_f 0.16 (benzene). IR spectrum 3400, 3100, 1780, 1620, 1575, 1535, 1350, 1255, 1205, 1090, 1050, 935, 855, 840, 795, and 730 cm^{-1}. Found, %: C 41.3, H 1.0, N 14.9. $C_{13}H_4N_4O_{10}$. Calculated, %: C 41.5, H 1.1, N 14.9.

2,4,8-Trinitro-6H-dibenzo[b,d]pyran-6-one (X). A 1.96-g (10 mmole) sample of III was added to 30 ml of nitric acid (sp. gr. 1.51), after which the mixture was refluxed for 2 h, cooled, and poured over ice. The precipitate was removed by filtration, washed with water and dried to give 3.04 g (92%) of X in the form of cream-colored crystals from acetic acid with mp 216-217°C (dec.) and R_f 0.6 [acetone—benzene (1:20)]. IR spectrum: 3400, 3080, 1770, 1620, 1550, 1530, 1360, 1270, 1205, 1110, 1050, 990, 915, 855, 840, 800, 785, 760, and 715 cm^{-1}. Found, %: C 47.0, H 1.4, N 12.7. $C_{13}H_5N_3O_8$. Calculated, %: C 47.1, H 1.5, N 12.7.

2-Hydroxy-2'-carboxy-3,5,4'-trinitrobiphenyl (XI). A 5.88-g (30 mmole) sample of III was added to a mixture from 12.6 ml of nitric acid (sp. gr. 1.51) and 98 ml of sulfuric acid (sp. gr. 1.84), and the resulting mixture was heated at 180°C for 4 h, after which it was cooled and poured over ice. The precipitate was removed by filtration, washed with water, and dried to give 4.47 g of a mixture of nitro compounds, which was treated three times with 50-ml portions of 5% sodium bicarbonate solution and filtered. The extracts were combined and heated with activated charcoal and filtered. Acetic acid was added to the filtrate, and the resulting precipitate was removed by filtration, washed with cold water, and dried to give 2.61 g (24%) of XI in the form of yellow needles from acetic acid with mp 210-212°C (dec.) and R_f 0.2 [acetone—benzene (1:3)]. IR spectrum: 3400, 3200, 3100, 1710, 1615, 1555, 1530, 1425, 1345, 1250, 1150, 1105, 1090, 1070, 940, 920, 865, 810, 775, 745, and 720 cm^{-1}. Found, %: C 43.4, H 2.0, N 11.75. $C_{13}H_7N_3O_9$. Calculated, %: C 43.45, H 2.0, N 11.7. The residue after extraction with sodium carbonate was recrystallized from acetic acid to give 1.74 g (17%) of X, which was identical to the sample obtained in the preceding experiment.

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

UDC 547.841'491:541.63

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

---

*The author sincerely thanks A. I. Kol'tsov for his assistance in recording and interpreting the PMR spectra.

N. N. Petrov Scientific-Research Institute of Oncology, Ministry of Public Health of the USSR, Leningrad 188646. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 468-473, April, 1985. Original article submitted July 26, 1984.

0009-3122/85/2104-0387$09.50