LITERATURE CITED

1. J. Harborne, The Biochemistry of Phenolic Compounds, Academic Press (1964).
2. G. N. Dorofeenko, V. V. Tkachenko, and V. V. Mezheritskii, Zh. Org. Khim., 12, 432 (1976).
3. G. N. Dorofeenko, V. V. Tkachenko, V. I. Yakovenko, V. V. Mezheritskii, and É. T. Oganesyan, Khim. Geterotsikl. Soedin., No. 2, 187 (1977).
4. G. N. Dorofeenko and V. V. Tkachenko, Zh. Org. Khim., 8, 2202 (1972).
5. M. A. Smith, R. M. Neumann, and R. A. Webb, J. Heterocycl. Chem., 5, 425 (1968).

CHARACTER OF THE PRODUCTS OF BROMINATION OF 1,3-DIOXACYCLANES WITH N-BROMOSUCCINIMIDE

S. A. Kotlyar and G. L. Kamalov

UDC 547.892'841'729.7:542.944.2

The dependence of the character and composition of the products of the reaction of equimolar amounts of N-bromosuccinimide and 1,3-dioxacyclanes on the ring size and the character of the substituent in the 2 position of the 1,3-dioxacyclane ring was examined. Reasons for the primary formation of bromination products of different types for five-, six-, and seven-membered cyclic acetals are proposed.

It is known that acyclic acetals undergo virtually quantitative bromination by N-bromosuccinimide (NBS) to the corresponding α-bromoacetals [1], whereas this reaction pathway is not characteristic for 2-alkyl-1,3-dioxalanes and 1,3-dioxanes [2, 3], and they form primarily the corresponding bromoalkyl esters of carboxylic acids.

We have examined the dependence of the character and composition of the products of the reaction of 1,3-dioxacyclanes with an equimolar amount of NBS on the ring size and the nature of the substituents in the 2 position. The bromination was carried out in CCl_4 solution without traces of peroxide at 20-70°C. As expected, 4-bromobutyl esters of formic and benzoic acids, respectively, are formed in up to 75% yields in the case of 1,3-dioxepane and 2-phenyl-1,3-dioxepane at 70°C, while the bromination of 2,2-dimethyl-1,3-dioxane (40°C) leads exclusively to 2-methyl-2-bromomethyl-1,3-dioxane in 80% yield.

However, we were able to detect substantial differences in the primary reaction pathway as a function of the ring size in the case of dioxacyclanes with the general formula $\mathrm{CH_3\overline{CHOCH_2(CH_2)_{\mathit{n}}CH_2O}}$. The compositions (in %) and the character of the reaction determined by gas–liquid chromatography (GLC) are presented in Table 1, in which I is $\mathrm{BrCH_2\overline{CHOCH_2(CH_2)_{\mathit{n}}CH_2O}}$, , II is $CH_3COOCH_2(CH_2)_nCH_2Br$, and III are unidentified products.

In the case of 2-butyl-1,3-dioxepane the I:II:III ratio at 70°C is 65:20:15. Irradiation of the reaction mixture at 20°C with a 60-W lamp in the case of 2-methyl-1,3-dioxepane

TABLE 1. Compositions of the Products of Bromination of 1,3-Dioxacyclanes

n	t, °C	I	II	III
0	70	0	85	15
1	40	20	80	—
1	70	14	86	—
2	40	80	10	10
2	70	53	25	22

Physicochemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 174-175, February, 1981. Original article submitted November 2, 1979.

0009-3122/81/1702-0118$07.50

makes it possible to preparatively synthesize the corresponding bromide I in 65% yield; only traces of alternative ester II were detected.

The results obtained in this research can most likely be explained by the higher stability of the corresponding 2-(1,3-dioxacyclo)alkyl radicals when n = 0, 1, and as a consequence, by the greater ease of isomerization of these radicals to acetoxyalkyl radicals which lead to the corresponding bromoalkyl esters. On the other hand, 2-alkyl-1,3-dioxepanes resemble acyclic acetals to a greater extent in their reactions with NBS, and thus the direction of the bromination of cyclic acetals changes substantially on passing from a six-membered ring to a seven-membered ring. Let us note that the corresponding bromide I is formed primarily in the bromination of 2-alkyl-1,3-dioxacyclanes with 1,4-dioxane dibromide, regardless of the size of the ring [4, 5].

In analogy with the results in [6], it may be assumed that III are either the corresponding chloro derivatives, which may be due to the participation of CCl_4 in chain propagation, or products of the reaction of the hydrogen bromide that is observed in small amounts with the starting compounds, as well as with I and II.

EXPERIMENTAL

A mixture of 0.1-mole of 1,3-dioxacyclane and 0.1-mole of NBS in 100-ml of CCl_4 was stirred in a thermostatted reactor until it became completely colorless. The liberated succinimide was removed by filtration, the solvent was removed by distillation at reduced pressure, and the residue was analyzed by gas—liquid chromatography (LKhM-7A, E-301, SKTFT-50, helium, 100-140°C, catharometer) and fractionated *in vacuo*. Alternative reaction products I and II were identified by alternative synthesis by known methods [7-9].

LITERATURE CITED

1. E. N. Marvell and M. J. Joncich, J. Am. Chem. Soc., 73, 973 (1951).
2. J. Gelas and S. Michaud, Bull. Soc. Chim. Fr., No. 7, 2445 (1972).
3. A. Bazbouz, J. Coste, H. Christol, and F. Plenat, Tetrahedron Lett., No. 1, 11 (1979).
4. A. V. Bogatskii, G. L. Kamalov, S. A. Kotlyar, N. G. Luk'yanenko, and G. Raif, Dokl. Akad. Nauk SSSR, 237, 338 (1977).
5. A. V. Bogatskii, G. L. Kamalov, S. A. Kotlyar, N. G. Luk'yanenko, and G. Raif, Khim. Geterotsikl. Soedin., No. 1, 131 (1978).
6. F. W. Baker, H. D. Holtz, and L. M. Stock, J. Org. Chem., 28, 514 (1963).
7. A. V. Bogatskii (Bogatsky), G. L. Kamalov, N. G. Luk'yanenko (Lukjanenko), S. A. Kotlyar (Kotljar), M. Bartok, J. Thsombosh, and Yu. Yu. Samitov, Acta Chim. Acad. Sci. Hung., 86, 173 (1975).
8. S. Secler, J. Org. Chem., 24, 1839 (1959).
9. B. G. Pishnamazzade and N. N. Nabiev, Azerb. Khim. Zh., No. 1, 92 (1971).