Figure 2 represents a separation of the space into the regions: 1) amines; 2) difluoroamines; 3) diaziridines; 4) nitramines; 5) aliphatic NC; 6) unsaturated NC; 7) aromatic NC; 8) anions of NC; 9) alicyclic NC; 10) α-fluoronitroalkanes.

The charge on the N atom in the nitrogen-containing compounds studied by us varies within wide limits: from +0.6 to −0.4 ecu, i.e., ~1 ecu. Despite this, nitrogen compounds occupy a small region of the space, which is bounded by the extreme values of the charges on the N atom and the atoms surrounding it, whereas each class has a region that is characteristic for it.

A statistical treatment of the results based on the principle of finding the average vector for each class of nitrogen compounds and the average deviations for each coordinate of a four-dimensional space (Table 2) gives a satisfactory separation of the classes. Besides this, the regions also differ in the density of the points, which was determined as $\rho = \frac{n}{\sqrt{\Delta q_N^2 + \Delta q_{\max}^2 + \Delta q_{\min}^2 + \Delta q^2}}$ for each class of compounds.

As a result, the molecules of nitrogen-containing compounds can be separated into classes on the basis of the data concerning the electronic structure of the $C-NO_2$ fragments, or in the general case of NX_3.

CONCLUSIONS

It was shown that it is theoretically possible to classify nitrogen-containing compounds on the basis of the obtained quantum-chemical data concerning their electronic structure.

LITERATURE CITED

1. A. V. Belik, R. Z. Zakharyan, and V. A. Shlyapochnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1714.
2. A. V. Belik, S. K. Bakeeva, and V. A. Shlyapochnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 2608.
3. H. D. Hess, A. Bander, and H. H. Gunthard, J. Mol. Spectrosc., 22, 208 (1967).
4. J. H. Hog, L. Hygard, and G. O. Sorensen, J. Mol. Struct., 7, 111 (1971).
5. A. S. Skapski and J. L. Stevenson, J. Chem. Soc., Perkin Trans. 2, 1967, 1197.
6. K. M. Trueblood, E. Goldisch, and J. Dononue, Acta Cryst., 14, 1009 (1961).

SYNTHESIS OF ROSEFURAN FROM CITRAL

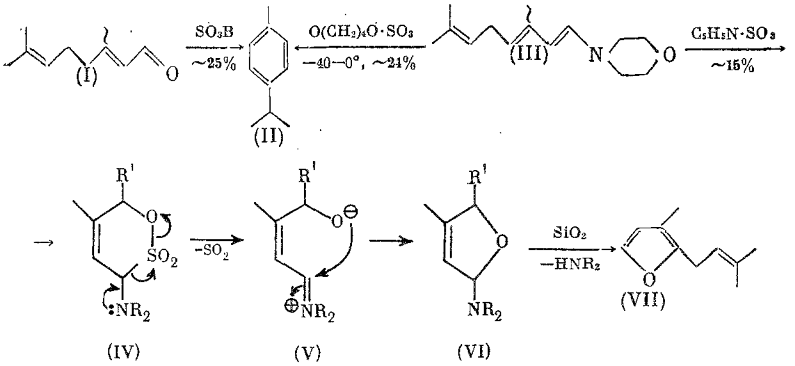
I. M. Zaks and A. M. Moiseenkov UDC 542.91:547.382.2:541.49:547.821:546.226-31

Recently, we described the synthesis of β,γ-unsaturated δ-sultones from 1,3-dienes and donor–acceptor SO_3 complexes [1]. In the present paper is discussed the possibility of accomplishing a similar cycloaddition involving citral (I) and the appropriate dienamines.

Depending on the conditions, it is known that when various electrophilic agents act on (I), its Schiff bases, enol ethers, and related dienamines they undergo either p-menthane cyclization or are converted to cyclocitral derivatives [2, 3]. As it proved, the previously unstudied reaction of (I) (E/Z = 3 : 2) with either the dioxane- or pyridinesulfotrioxides gives under the conditions of [1] p-cymene (II) as the main identified product. We also detected the latter after treating (I) with an $H_2SO_4-Ac_2O$ mixture under the conditions of forming heteroorganic δ-sultones from conjugated carbonyl compounds [4].

The reaction of the readily available [3] amino derivatives of citral of the morpholine dienamine (III) type (mixture of E/Z isomers of unestablished composition) with the mentioned SO_3 complexes was not studied previously. We found that dioxanesulfotrioxide under various conditions causes substantial tarring of (III) and the simultaneous formation of (II) in low yield. In the case of $Py \cdot SO_3$, together with a small amount of (II), we unexpectedly isolated a product that was devoid of sulfur and nitrogen, which in its properties coincided with an authentic specimen of rosefuran (VII), a component of ethereal rose oil [5]. The structure of (VII) was confirmed by comparing its PMR spectrum with that described for synthetic [5, 6] rosefuran:

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2614-2615, November, 1982. Original article submitted April 13, 1982.



The yield of furanomonoterpene (VII) under the found conditions does not exceed 15%, and its formation can be explained on the basis of the probable intermediate aminosultone (IV). The possible reductive conversion of the latter to betaine (V) postulates the formation of dihydrofuran (VI), which, in turn, is capable of aromization under the adopted conditions of working up the reaction mixture, including its chromatography on SiO_2.

EXPERIMENTAL

p-Cymene (II). To a suspension of dioxanesulfotrioxide, obtained at −20° C from 2 g (25 mmoles) of SO_3 and 2.5 ml (29 mmoles) of dioxane in 20 ml of CH_2Cl_2, stirred in an argon atmosphere, was added 4.5 ml (26 mmoles) of (I) in 10 ml of CH_2Cl_2 in 10 min at −40°. The reaction mass was warmed up to 0° in 40 min, kept for 1 h at 0°, and then it was treated with ether. The obtained solution was washed with H_2O, neutralized with $NaHCO_3$, dried over Na_2SO_4, and evaporated in vacuo. The tarry residue (2.8 g) was chromatographed on 70 g of SiO_2. Elution with a 10 :1 hexane−ether mixture gave 0.81 g (25%) of substance, which was identical (GLC, PMR) with authentic (II).

In a similar manner, from 1.8 g (22.5 mmoles) of SO_3, 2.0 ml (25 mmoles) of Py, and 4.1 ml (24 mmoles) of citral in 25 ml of CH_2Cl_2, after chromatography (2.5 g of substance, 80 g of SiO_2), we obtained 0.88 g (30%) of (II).

Rosefuran (VII). In a similar manner, from 1.5 g (18.8 mmoles) of SO_3, 1.6 ml (20.6 mmoles) of Py, and 4.25 g (19.3 mmoles) of (III) [3] in 30 ml of CH_2Cl_2, after chromatography (2.3 g of substance, 50 g of SiO_2), we obtained 0.38 g (13.5%) of (VII), bp 41° (1 mm), which by GLC was shown to be identical with authentic rosefuran. PMR spectrum (CCl_4, δ, ppm): 1.69 br.s (6H, CH_3); 1.92 br.s (3H, CH_2-C^3); 3.20 d (2H, CH_2, J = 7.5 Hz); 5.23 br.s (1H, HC=C, J = 7.5 Hz); 6.02 d (1H, HC^4, J = 2 Hz); 7.10 d (1H, HC^5, J = 2 Hz). Found: C 79.98; H 9.39%; M^+ 150. $C_{10}H_{14}O$. Calculated: C 79.95; H 9.39%; mol. wt. 150.2.

CONCLUSIONS

The action of pyridinesulfotrioxide causes the conversion of the morpholine derivative of citral to rosefuran.

LITERATURE CITED

1. A. V. Semenovskii, E. V. Polunin, I. M. Zaks, and A. M. Moiseenkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 1327.
2. V. A. Smit and V. F. Kucherov, Usp. Khim., 28, 272 (1959).
3. M. Shibasaki, S. Terashima, and S. Yamada, Chem. Pharm. Bull., 23, 272, 279 (1975).
4. S. H. Doss and S. R. Michael, Rev. Roum. Chim., 24, 605 (1979).
5. G. Buchi, Sr., E. Kovats, P. Enggist, and G. Uhde, J. Org. Chem., 33, 1227 (1968).
6. A. Takeda, K. Shinhama, and S. Tsuboi, Bull. Chem. Soc. Jpn., 50, 1903 (1977).