9. J. Albertsson, A. Oskarsson, and K. Stahl, Acta Chem. Scand., Ser. A, 36, 783 (1982).
10. H. Iwasaki and K. Kobayashi, Acta Cryst., Sect. B, 36, 1655 (1980).
11. B. Bak, D. Christensen, J. Rastrup-Andersen, and E. Tannenbaum, J. Chem. Phys., 25, 892 (1956).
12. Ya. L. Gol'dfarb, A. A. Dudinov, V. P. Litvinov, D. S. Yufit, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 10, 1326 (1982).
13. B. P. Fedorov, G. I. Gorushkina and Ya. L. Gol'dfarb, Zh. Org. Khim., 1, 777 (1965).
14. A. N. Zverev and V. G. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2440 (1973).
15. R. Chant, A. R. Hendrickson, R. Z. Martin, and N. M. Rohde, Austral. J. Chem., 26, 2533 (1973).
16. N. A. Ulakhovich, G. K. Budnikov, and L. G. Fomina, Zh. Obshch. Khim., 50, 1620 (1980).
17. G. K. Budnikov, N. A. Ulakhovich, O. Yu. Kargina, and L. G. Fomina, Zh. Obshch. Khim., 48, 1667 (1978).
18. A. R. Hendrickson, R. Z. Martin, and N. M. Rohde, Inorg. Chem., 14, 2980 (1975).
19. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).
20. A. Reiche, H. Gross, and U. Hoft, Chem. Ber., 93, 88 (1960).
21. W. Huber, J. Am. Chem. Soc., 66, 876 (1944).
22. S. J. Lukasiewicz and E. H. Murray, J. Am. Chem. Soc., 68, 1389 (1946).

PECULIARITIES OF THE STEREOCHEMISTRY OF THE DISPROPORTIONATION, IONIC, AND CATALYTIC HYDROGENATION OF POLYSUBSTITUTED 4H-THIOPYRANS

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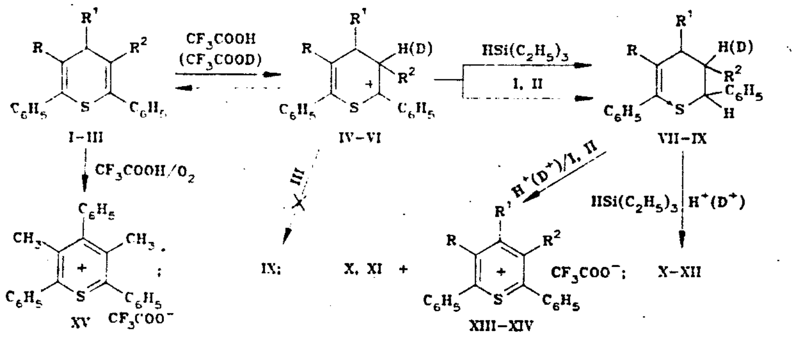
UDC 547.818.1:542.942.7:543.422.25

The configuration of the thiacyclohexane obtained in the ionic and catalytic hydrogenation of 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran was established. It is shown that the stereochemistry of these reactions differs for penta- and tetrasubstituted 4H-thiopyrans in that the stereochemistry of the cited processes and the stereochemistry of disproportionation are the same for each of the polysubstituted 4H-thiopyrans.

In contrast to tetrasubstituted 4H-thiopyrans I and II, 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran (III) does not disproportionate with trifluoroacetic acid but is converted quantitatively to thiopyrylium trifluoroacetate XV with the participation of oxygen [1]:



I, IV, VII, X, XIII $R=CH_3$, $R'=C_6H_5$, $R^2=H$; II, V, VIII, XI, XIV $R=R^2=CH_3$, $R'=H$; III, VI, IX, XII $R=R^2=CH_3$, $R^1=C_6H_5$.

3,5-Dimethyl-2,4,6-triphenylthiacyclohexane (XII), which should be formed in the case of disproportionation of thiopyran III, can be obtained only by the action of the $CF_3COOH/HSi(C_2H_5)_3$ hydrogenating pair on this unsaturated sulfide or as a result of its catalytic hydro-

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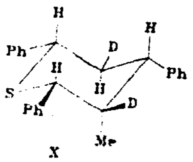
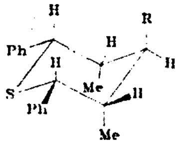
0009-3122/87/2307-0747$12.50

genation (H_2, Pd/C). The same isomer of thiacyclohexane XII is obtained in both cases; this is characteristic for the disproportionation and ionic and catalytic hydrogenation of substituted 4H-thiopyrans, including thiopyrans I and II [2, 3]. Sulfide XII, like XI, has a fixed chair conformation with equatorial phenyl substituents attached to the $C_{(2)}$ and $C_{(6)}$ atoms and axial methyl groups attached to the $C_{(3)}$ and $C_{(5)}$ atoms [3]. The chemical shift of the protons of the indicated methyl substituents in the PMR spectrum of thiacyclohexane XII (0.86 ppm) is close to that in the spectrum of sulfide XI (0.9 ppm). At the same time, in the spectrum of thiacyclohexane X the signal of the protons of the axial methyl group attached to the $C_{(3)}$ atom, which experience the shielding effect of two vicinal phenyl rings [attached to the $C_{(2)}$ and $C_{(4)}$ atoms] that are equatorially oriented and are situated at an angle relative to the principal plane of the heteroring, is found at 0.67 ppm [2], i.e., at stronger field as compared with sulfides XI and XII. This makes it possible to draw a conclusion regarding the axial orientation of the phenyl substituent attached to the $C_{(4)}$ atom in thiacyclohexane XII. Although an axial orientation of the phenyl group in six-membered saturated carbo- and heterocycles is unlikely, examples of its realization are known [4, 5].



X



XI R=H; XII R=C_6H_5

The formation of thiacyclohexane XII in the reaction of thiopyran III with CF_3COOH in the presence of triethylsilane constitutes evidence that protonation of the double bonds of the heteroring of III occurs in the reaction with this acid. However, it is apparent from a comparison of the three-dimensional structures of I and III, which exist primarily in the boat form with a pseudoaxial phenyl group attached to the $C_{(4)}$ atom [6] and thiacyclohexanes X and XII obtained from them, carbonium ions IV and VI, which develop in the reaction of thiopyrans I and III with CF_3COOH or CF_3COOD, are destabilized as a consequence of steric interaction of the substituents attached to the $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ atoms. In addition, whereas attack by hydrogenating agents on the double bond of thiopyran I occurs on the "rear" side of the molecule, i.e., on the side opposite to the substituent attached to the $C_{(4)}$ atom, in the case of thiopyran I it is realized on the sterically hindered "front" side. As a result, thiopyran I disproportionates with trifluoroacetic acid, while thiopyran III reacts with it to form salt XV via a mechanism that competes with disproportionation.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Varian FT-80a spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard.

The catalytic hydrogenation of 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran (III) was accomplished by the method in [7]. Thiacyclohexane XII, with mp 112-113.5°C (111.5-112 C° [1]), was obtained in 64% yield.

LITERATURE CITED

1. V. G. Kharchenko and N. I. Kozhevnikova, Khim. Geterotsikl. Soedin., No. 2, 200 (1983).
2. V. G. Kharchenko and N. I. Kozhevnikova, in: Research on the Synthesis and Catalysis of Organic Compounds [in Russian], V. G. Kharchenko and Yu. N. Usov (eds.), Saratov State University, Saratov (1983), p. 19.
3. V. G. Kharchenko, N. I. Kozhevnikova, A. A. Shcherbakov, G. G. Aleksandrov, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 3, 324 (1980).
4. J. Stoddart, The Stereochemistry of Carbohydrates, Wiley (1971), p. 246.
5. N. Satuamurthy, R. Sivakumar, K. Ramalingam, K. D. Berlin, R. A. Loghry, and D. Helm, J. Org. Chem., 45, 349 (1980).
6. N. I. Kozhevnikova and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 8, 1042 (1985).
7. V. G. Kharchenko, K. S. Smirnova, S. N. Chalaya, A. S. Tatarinov, and L. G. Chichenkova, Zh. Org. Khim., 11, 1543 (1975).