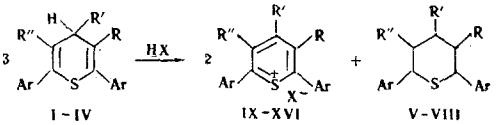
DISPROPORTIONATION OF γ-THIOPYRANS

V. G. Kharchenko, M. E. Stankevich,
A. R. Yakoreva, and E. G. Lilienfel'd

UDC 547.811

For the first time we have established the ability of γ-thiopyrans to disproportionate with hydrogen transfer under the influence of protic acids ($HClO_4$, HCl, CF_3COOH).



I-IV IX-XVI V-VIII

I, V, IX, X: Ar = R′ = C_6H_5, R = R″ = H; II, VI, XI: Ar = C_6H_5, R′ = H, R = R″ = CH_3; III, VII, XII, XIII, XIV: Ar = C_6H_5, R′ = CH_3, R = R″ = H; IV, VIII, XV, XVI: Ar = C_6H_5, R′ = $C_6H_4OCH_3$, R = R″ = H
IX, XII, XV: X^- = Cl^-; XI, XIII: X^- = ClO_4^-;
X, XIV, XVI: X^- = CF_3COO^-

The disproportionation of γ-thiopyrans reveals the mechanism of the formation of thiapyrylium salts by attesting to the fact that the carbonium ions arising during protonation of the double bonds of γ-thiopyrans are hydride-ion acceptors. The mechanism of the reaction is similar to the mechanism for disproportionation of α-thiochromenes [1] and symoctahydrothioxanthenes [2]. The established transformation opens a new path for the synthesis of substituted thiacyclohexanes.

The structures of the thiapyrylium salts were confirmed by mixed melting-point determinations with authentic thiapyrylium salt samples [3, 4] and by exchange reactions. The structures of the thiacyclohexanes were confirmed by the IR spectra and elementary analysis of the sulfides and sulfones. Compounds V-VIII do not contain absorption bands which correspond to double bonds and are readily and smoothly oxidized to sulfones by hydrogen peroxide.

EXPERIMENTAL

2,4,6-Triphenyl-1-thiacyclohexane (V). This was obtained in 20% yield and had mp 107-108° (from alcohol). Found %: C 83.52, 83.60; H 6.60, 6.54; S 9.60, 9.51. $C_{23}H_{22}S$. Calculated %: C 83.63; H 6.66; S 9.20.

2,4,6-Triphenyl-1-thiacyclohexane 1,1-Dioxide. This was obtained in 80% yield and had mp 272-274° (from alcohol). Found %: C 76.38, 76.32; H 6.48, 6.62; S 8.56, 8.62. $C_{23}H_{22}O_2S$. Calculated %: C 76.24; H 6.07; S 8.84.

2,6-Diphenyl-3,5-dimethyl-1-thiacyclohexane (VI). This was obtained in 25% yield and had mp 166-167° (from alcohol). Found %: C 80.83, 80.62; H 7.73, 7.93; S 11.16, 11.51. $C_{19}H_{22}S$. Calculated %: C 80.85; H 7.80; S 11.35.

2,6-Diphenyl-3,5-dimethyl-1-thiacyclohexane 1,1-Dioxide. This was obtained in 78.6% yield and had mp 254-255° (from alcohol). Found %: C 74.30, 74.38; H 7.43, 7.18; S 10.15, 10.13. $C_{19}H_{22}O_2S$. Calculated %: C 72.61; H 7.00; S 10.19.

2,6-Diphenyl-4-methyl-1-thiacyclohexane (VII). This was obtained in 26% yield and had mp 63-64° (from alcohol). Found %: C 80.32, 80.42; H 7.60, 7.67; S 11.85, 11.82. $C_{18}H_{20}S$. Calculated %: C 80.53; H 7.46; S 11.94.

Saratov Polytechnical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 422-423, March, 1971. Original article submitted April 27, 1970.

2,6-Diphenyl-4-methyl-1-thiacyclohexane 1,1-Dioxide. This was obtained in 92% yield and had mp 226-227° (from alcohol). Found %: C 71.58, 71.75; H 7.17, 6.78; S 10.52, 10.60. $C_{18}H_{20}O_2S$. Calculated %: C 72.00; H 6.66; S 10.66.

2,6-Diphenyl-4-(p-methoxyphenyl)-1-thiacyclohexane 1,1-Dioxide. 2,6-Diphenyl-4-(p-methoxyphenyl)-1-thiacyclohexane (VIII) was identified through its sulfone, which was obtained by oxidation with hydrogen peroxide of a reaction mixture consisting of uncrystallized product. The yield of the sulfone was calculated on the basis of the starting γ-thiopyran and was 16%. The product melted at 274-276° (from acetic acid). Found %: C 73.19, 73.03; H 6.24, 6.23; S 8.47, 8.36. $C_{24}H_{24}O_3S$. Calculated %: C 73.47; H 6.12; S 8.16.

The 2,4,6-triphenyl- (IX), 2,6-diphenyl-4-(p-methoxyphenyl)- (XV), and 2,6-diphenyl-4-methylthiapyrylium chlorides (XII) were identified by mixed melting-point determinations with authentic thiapyrylium chlorides [3]; 2,6-diphenyl-3,5-dimethyl- (XI) and 2,6-diphenyl-4-methylthiapyrylium perchlorates (XIII) [4] were similarly identified.

2,4,6-Triphenylthiapyrylium Trifluoroacetate (X). This was obtained in 60.6% yield and had mp 176-177°. The structure was confirmed by an exchange reaction with perchloric acid and a mixed melting-point determination with an authentic sample [5].

2,6-Diphenyl-4-methylthiapyrylium Trifluoroacetate (XIV). This was obtained in 62% yield and had mp 76-77° (decomp.). It was characterized via the iodide by an exchange reaction with KI. It did not depress the melting point of the authentic iodide [4].

2,6-Diphenyl-4-(p-methoxyphenyl)thiapyrylium Trifluoroacetate (XVI). This was obtained in 65% yield and had mp 133-134°. It was characterized through the perchlorate by an exchange reaction with $HClO_4$. It did not depress the melting point of the authentic perchlorate [5].

LITERATURE CITED

1. B. D. Tilak and V. M. Vaidya, Tetrahedron Lett., 489 (1963).
2. V. G. Kharchenko, S. K. Klimenko, and T. I. Krupina, Zh. Organ. Khim., 3, 1344 (1967).
3. V. G. Kharchenko, V. I. Kleimenova, N. M. Kupranets, N. V. Polikarpova, and A. R. Yakoreva, Zh. Organ. Khim., 4, 2054 (1968).
4. V. G. Kharchenko and V. I. Kleimenova, Materials of the 33rd Scientific-Technical Conference, Saratov [in Russian] (1970), p. 33.
5. R. Wizinger and P. Ulrich, Helv. Chim. Acta, 39, 207, 217 (1956).