3496 J. Org. Chem. 1982, 47, 3496-3497

Formation of 2*H*-Thiopyrans upon Reaction of Thiopyrylium Ions with Amines

Vincenzina Carla Cordischi, Giancarlo Doddi,* and Franco Stegel*

Centro CNR di Studio sui Meccanismi di Reazione, c/o Istituto di Chimica Organica, Università di Roma, 00185 Roma, Italy

Received January 7, 1982

2*H*-Thiopyrans are detected by ^{1}H and ^{13}C NMR spectroscopy as the products of primary interaction of 2,4-diphenyl- and 2,4,6-triphenylthiopyrylium ions with amines. This behavior is at variance with that presently reported for this kind of reaction and in contrast with that observed in the reactions of pyrylium ions, where 2*H*-pyrans can be detected in particular cases only. With primary amines the final products of the thiopyrylium ion reactions are 1-substituted pyridinium ions, which are formed according to a reaction course common to pyrylium and thiopyrylium ions.

The reactions of 2,4,6-triphenylthiopyrylium (1) and 2,4-diphenylthiopyrylium (2) perchlorates with primary and secondary amines in Me$_2$SO-d_6 and/or CD$_3$CN were studied by ^{1}H and ^{13}C NMR spectroscopy at 25 ± 1 °C.

The addition of 2 equiv of butylamine to a solution of 300 mg of 1 in 2 mL of Me$_2$SO-d_6 leads to the complete disappearance of the ^{13}C spectrum of the starting cation, as characterized by the low field C-α and C-γ signals (δ 161.1 and 160.7, respectively), and to the formation of the 2*H*-thiopyran adduct **3**, whose characterizing features are the nonequivalence of the C-3 and C-5 carbon atoms (δ 122 and 117.3) and the presence of the C-2 signal at δ 74.5.[1] This signal is not split in off-resonance-decoupling experiments and is situated strongly upfield with respect to the corresponding signal of the substrate. The absence of any other signals, except those of phenyl groups, indicates that **3** is the only product.

Also the ^{1}H NMR spectra obtained in Me$_2$SO-d_6 and CD$_3$CN are in agreement with the formation of adduct **3**. Interestingly, the ^{1}H NMR spectrum, as recorded immediately after the addition of butylamine in Me$_2$SO-d_6, shows the presence of a weak singlet, besides the signals of **3**, at δ 6.0, where a 4*H*-thiopyran is expected to absorb.[2] Experiments carried out with OH$^-$ rule out any interference of this ion, which would result from the reaction of the amine with any water in the solvent. After a few minutes the signal at δ 6.0 disappears in correspondence to an increase of the signals of **3**. No evidence was obtained for the presence of a thiabenzene derivative, which would be expected to display an NMR signal at δ >7.[3] Similar behavior had already been observed in the reaction of 1 with CH$_3$O$^-$ ion and was ascribed to the transient formation of a 4*H*-thiopyran adduct.[4] A detailed kinetic study of this reaction has indeed shown that the 4*H*-thiopyran adduct is the kinetically favored isomer whereas the 2*H* adduct is the thermodynamically more stable one.[5]

2*H*-Thiopyrans were also obtained from the corresponding reaction of 1 with secondary or primary amines other than butylamine. The related ^{1}H NMR chemical shift values are reported in Table I. With aniline the corresponding 2*H* adduct is observed only after the addition of 1 equiv of triethylamine.

Chart I

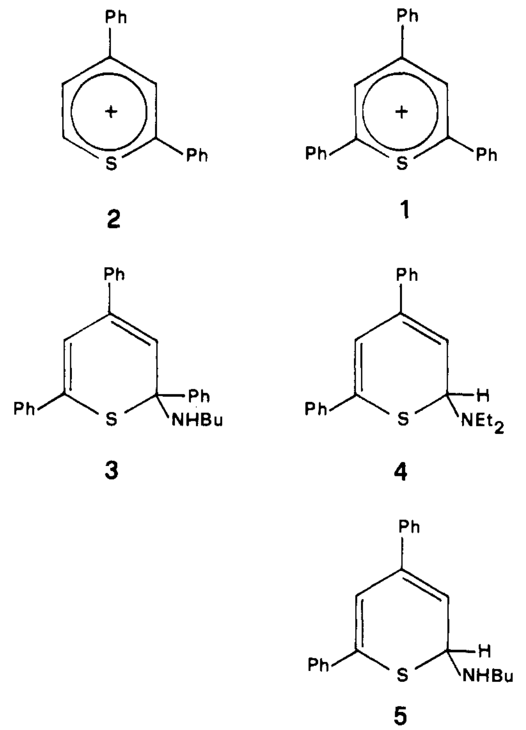

Table I. ^{1}H NMR Characterizing Chemical Shifts for 2,4,6-Triphenylthiopyrylium Ion (1) and Related 2*H*-Thiopyran Adducts with Amines

compd	solvent	chemical shift, δ H-3	chemical shift, δ H-5	$J_{3,5}$, Hz
1	Me$_2$SO-d_6	9.30	9.30	
	CD$_3$CN	9.05	9.05	
1 + butylamine (3)	Me$_2$SO-d_6	5.70	6.95	0.5
1 + *tert*-butylamine	Me$_2$SO-d_6	6.01	7.07	0.5
1 + aniline	Me$_2$SO-d_6	5.95	7.05	0.5
1 + methylamine	CD$_3$CN	5.81	7.03	0.5
1 + propylamine	CD$_3$CN	5.78	7.01	0.5
1 + piperidine	Me$_2$SO-d_6	5.70	6.77	0.5
1 + diethylamine	Me$_2$SO-d_6	5.88	6.76	0.5
	CD$_3$CN	5.85	6.65	0.5

After some days at room temperature the ^{1}H NMR signals of the 2*H* adducts formed with primary amines undergo a broadening, and eventually the signals of the 1-alkyl(aryl)-2,4,6-triphenylpyridinium ions are observed.[6]

---

[1] The assignments for C-3, C-4, C-5, and C-6 carbon atoms were allowed by comparison with the ^{13}C NMR spectrum of 2-methoxy-2,4,6-triphenyl-2*H*-pyran: Katritzky, A. R.; Brownlee, R. T. C.; Musumarra, G. *Heterocycles* **1979**, *12*, 775.

[2] (a) Maryanoff, B. E.; Stackhouse, J.; Senkler, G. H., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 2718. (b) Chen, C. H.; Doney, J. J.; Reynolds, G. A. *J. Org. Chem.* **1982**, *47*, 680.

[3] Suld, G.; Price, C. C. *J. Am. Chem. Soc.* **1962**, *84*, 2090.

[4] Aveta, R.; Doddi, G.; Insam, N.; Stegel, F. *J. Org. Chem.* **1980**, *45*, 5160.

[5] Doddi, G.; Illuminati, G.; Insam, N.; Stegel, F. *J. Org. Chem.* **1982**, *47*, 960.

[6] Formation of 1-methyl-2,4,6-triphenylpyridinium ion from reaction of 1 with methylamine in MeOH was also reported in: Yoshida, Z.; Sugimoto, H.; Sugimoto, T.; Yoneda, S. *J. Org. Chem.* **1973**, *38*, 3990.

0022-3263/82/1947-3496$01.25/0

Table II. ^{1}H NMR Characterizing Chemical Shifts for 2,4-Diphenylthiopyrylium Ion (2) and Related 2*H*-Thiopyran Adducts with Amines

compd	solvent	chemical shift, δ H-3	H-5	H-6	$J_{3,5}$, Hz	$J_{5,6}$, Hz	$J_{3,6}$, Hz
2	CD_3CN	9.07	8.95	9.84	1.5	9.0	0

compd	solvent	chemical shift, δ H-2	H-3	H-5	$J_{2,3}$, Hz	$J_{2,5}$, Hz	$J_{3,5}$, Hz
2 + diethylamine (4)	CD_3CN	5.35	5.85	6.85	6.7	0	0.5
2 + butylamine (5)	CD_3CN	5.25	5.80	6.85	7.5	0	0.5

The formation of 2*H*-thiopyran adduct 4 is observed in the reaction of 2 with diethylamine in CD_3CN by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum obtained upon addition of 2 equiv of diethylamine to a solution of 300 mg of **2** in 2 mL of CD_3CN shows a strong upfield shift of the hydrogen-bearing α-carbon atom (from δ 154.2 to 65.3), because of the neutralization of the positive charge and the change of hybridization from sp^2 to sp^3. In off-resonance-decoupling experiments this signal is detected as a doublet. The corresponding ^{1}H NMR chemical shift values are reported in Table II.

The ^{1}H NMR spectrum obtained for the corresponding reaction with butylamine in CD_3CN shows the presence of the signals of the 2*H* adduct **5** (see Table II) together with the signals of another compound (δ 4.83, d, $J = 6.7$ Hz; δ 6.05, slightly broadened doublet, $J = 6.7$ Hz; δ 6.96, slightly broadened singlet). The latter signals undergo a slow increase with time, whereas those of the 2*H* adduct show a corresponding decrease. The ^{13}C NMR spectrum of this reaction mixture is rather complicated. However, a distinctive feature is the presence of a weak signal at δ 214.3, which may be attributed to a thiocarbonyl group, suggesting the presence of ring opening to a divinylogous thioamide structure for this compound. The final product of this reaction is 1-butyl-2,4-diphenylpyrydinium ion as formed according to an already known reaction course.[7]

The behavior of thiopyrylium ions **1** and **2** toward amines reported here is in contrast with that of the unsubstituted thiopyrylium ion, which reacts with primary and secondary amines to yield open-chain cations,[6] and with that of the corresponding 2,4,6-triphenyl-[8] and 2,4-diphenylpyrylium ions,[9] where only the open-chain divinylogous amide or the final 1-substituted pyridinium ions are detected.

2*H*-Pyran adducts obtained from amines can be indeed observed in specific cases only, e.g., from sterically hindered[10] or 4-dialkylamino-substituted pyrylium ions.[11] Thus the ring-opening step is strongly affected by the substituents on the ring. Moreover, the presence of a sulfur atom seems to be a main factor in strongly depressing the rate of this step.

Experimental Section

^{1}H NMR measurements were carried out on a JEOL C60-HL instrument. ^{13}C NMR measurements were carried out on a Varian CFT-20 instrument. The temperature of the probe was kept at 25 ± 1 °C. The chemical shift values are quoted in δ units relative to Me_4Si. Me_2SO-d_6 and CD_3CN were standard grade solvents.

2,4,6-Triphenylthiopyrylium (1) perchlorate was available from a previous work.[5]

2,4-Diphenylthiopyrylium (2) perchlorate was prepared according to a literature procedure.[7]

Registry No. 1 ClO_4^-, 2930-37-2; 2 ClO_4^-, 30235-02-0; 3, 82338-23-6; 4, 82388-24-7; 5, 82388-25-8; diethylamine, 109-89-7; butylamine, 109-73-9.

---

[7] Graphakos, B. J.; Katritzky, A. R.; Lhommet, G.; Reynolds, K. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1345.

[8] Katritzky, A. R.; Brownlee, R. T. C.; Musumarra, G. *Tetrahedron* **1980**, *36*, 1643.

[9] Doddi, G., unpublished results.

[10] (a) Fisher, G. H.; Zimmermann, T. *Z. Chem.* **1981**, *21*, 282. (b) Katritzky, A. R.; Lloyd, J. M.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 1* **1982**, 117.

[11] Van Allan, J. A.; Reynolds, G. A.; Petropoulos, C. C. *J. Heterocycl. Chem.* **1972**, *9*, 783.

Flash Vacuum Pyrolysis of Substituted Pyridine *N*-Oxides and Its Application to Syntheses of Heterocyclic Compounds[1]

Akio Ohsawa, Takayuki Kawaguchi, and Hiroshi Igeta*

School of Pharmaceutical Sciences, Showa University, Shinagawa-ku, Tokyo 142, Japan

Received February 4, 1982

Flash vacuum pyrolysis of 2-picoline *N*-oxide gave 2-picoline, pyridine, 2-ethylpyridine, 2-vinylpyridine, 2-pyridylmethanol, bis(2-pyridyl)methane, 1,2-bis(2-pyridyl)ethane, and 1,2-bis(2-pyridyl)ethylene. These reactions are explained by intermediary participation of the 2-picolyl radical. Flash vacuum pyrolysis of methyl-substituted 2-benzylpyridine *N*-oxides led to methyl-substituted pyrido[1,2-*a*]indoles or to benzo[*g*]quinoline in moderate yields.

Although photochemical reactions of *N*-oxides of pyridine derivatives have been widely investigated,[2] little is known concerning the behavior of thermally excited molecules of these compounds. Flash vacuum pyrolysis

0022-3263/82/1947-3497$01.25/0