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Pyrylium Salts. Part VII.* A Derivative of *anti*-1,5:6,10-Bisepithiocyclodecene

SIGURD BAKLIEN, PER GROTH and KJELL UNDHEIM

Department of Chemistry, University of Oslo, Oslo 3, Norway

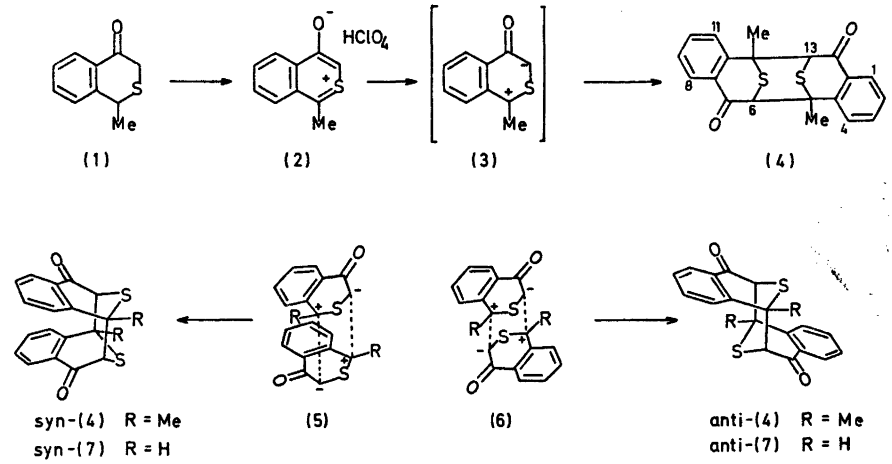
The perchloric acid salt of 1-methyl-2-benzothiopyrylium-4-olate has been obtained from 1-methylisothiochroman-4-one. The pyrylium salt is rapidly dimerised in the presence of a base. From spectroscopic and single crystal X-ray data the product has been identified as *anti*-5,12-dimethyl-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo[*a*,*f*]cyclodecene-7,14-dione.

1,3-Dipolar character has been demonstrated for pyridinium-3-olates [2] and *N*-methylisoquinolium-4-olate [3] by cycloaddition reactions under forcing conditions. The aromatically less stabilised isoelectronic 2-benzothiopyrylium-4-olate, however, undergoes preferential 1,3-dimerisation to the bisepithiocyclodecene (*7*),[4] while the dimerisation of the parent, thiopyrylium-3-olate and its 5-methyl derivative takes another course.[1] 2-Benzopyrylium-4-olate which is the least aromatically stabilised member of the present hetero-analogue series, has yielded some 1,3-dimerised product besides polymeric material.[5] Stabilisation of the pyrylium system by phenyl group substitution such as in 1,3-diphenyl-2-benzopyrylium-4-olate, which is formed by valence isomerisation of 2,3-epoxy-2,3-diphenylindan-1-one, results in derivatives which will behave as 1,3-dipolar reactants.[6] Photolysis of 2,3-epoxy-2-methyl-3-phenylindan-1-one, however, has yielded a minor dimeric by-product for which the substituted dioxa-analogue of (*7*) was suggested without specification of the stereoisomer involved.[7] The *syn*:*anti*-isomer ratio for (*7*) was about 7:1 in the formation from 2-benzothiopyrylium-4-olate;[4] the *syn*-isomer was also the major product in the dimerisation of thiopyrylium-3-olate and its 5-methyl analogue.[1] The *anti*-isomer, however, is probably thermodynamically more stable because of less non-bonded interaction. X-Ray data of *syn*-(*7*) show short interplanar distances and stretching of the C5—C6 and C12—C13 bonds implying repulsion between the periplanar faces.[8]

The directional face-to-face dimerisation can be visualised through the electron density distribution as indicated by the charges in structures (*5*) and (*6*). The incipient positive charge on C1 is stabilised by the fused benzo group. In this work we have studied the effect of an electron donating 1-substituent on the reactivity. For this purpose 1-methylbenzo[*c*]-thiopyrylium-4-olate (*2*) was synthesised and its dimerisation studied. The 1-methyl derivative (*2*) was prepared by hydride abstraction from 1-methylisothiochroman-4-one (*1*) by means of triphenylmethyl perchlorate as previously reported in the syntheses of some of its analogues.[1,4] (*1*) can be prepared by cyclisation of (1-phenylethylthio)acetic acid *via* its acid chloride under Friedel-Crafts conditions [9] or from the acid by means of phosphorus pentoxide as reported [10] for isothiochroman-4-one. The yields, however, are low because of the easy cleavage of the benzylic sulfide bond. The recently reported [11] cyclisation of [1-(2-carboxyphenyl)ethylthio]acetic acid under alkaline conditions circumvents the ready acid-catalysed benzyl thioether cleavage.

The structure of the thiopyrylium betaine (*2*) isolated as the perchloric acid salt is evident from spectroscopic data. The NMR spectrum (CD_3CN) has a methyl proton singlet at δ 3.4

* For Part VI, see Ref. 1.



Scheme 1.

and otherwise only aromatic protons; The UV spectrum (MeCN) has several absorption maxima with the highest wavelength band at 392 nm.

Treatment of the perchloric acid salt (*2*) dissolved in THF with triethylamine smoothly gave the dimeric product (*4*) at room temperature. UV absorptions recorded for a reaction run at −60 °C showed the disappearance of the longwave 392 nm band of the perchloric acid salt (*2*) with the transient appearance of a longwave band at *ca.* 450 nm; the latter is attributed to the intermediate thiopyrylium betaine. The progress of the reaction was also evident by the fading of the greenish-yellow colour of the solution. It is apparent that the methyl substituent has decreased the rate of dimerisation in comparison with the unsubstituted betaine. The reaction gave essentially one product. The molecular ion at *m/e* 352 confirms dimerisation. The NMR spectrum (DMSO-d_6) has the six protons for Me-5 and Me-12 as a singlet at δ 1.5 and H-6 and H-13 as a singlet at δ 4.0. In the unsubstituted dimer (*7*) the methine proton signals are split by 2 Hz ascribed to coupling between the methine protons on either side of the sulfur bridge.[4] Two of the aromatic protons resonate in the region δ 7.9 − 8.2 while the remaining aromatic proton signals are in the region δ 7.5 − 7.7. The lower field signals are ascribed to the aromatic protons in the *ortho*-position to the carbonyl groups. In the parent analogue (*7*) the corresponding protons in the *anti*-isomer resonate at lower fields than the other aromatic protons which was ascribed to the carbonyl anisotropy effect; these protons in the *syn*-isomer are in the aromatic shielding zone and therefore resonate at higher fields.[4] The NMR data are thus in accordance with formation of the *anti*-isomer which was confirmed by single crystal X-ray analysis. The oscillation diagram showed no symmetry. Zero-level Weissenberg diagram showed plane group *pgg* and the space group is therefore uniquely determined to be $P2_1/c$. Measurements on the films gave $a = 7.46$ Å, $b = 10.60$ Å and c sin $\beta = 10.33$ Å. The corresponding unit cell volume is $V = 817$ Å^3. The calculated density with two molecules in the cell is 1.44 g/cm^3 ($\varrho_{obs} \sim 1.45$ g/cm^3). For an *ordered* structure in space group $P2_1/c$ two molecules per unit cell are possible if and only if the molecules themselves possess a centre of symmetry which shows that the dimer must be the *anti*-isomer.

The base peak in the mass spectrum was at *m/e* 177 ($C_{10}H_9OS$); the relative intensities for the molecular ion and the ions at half of its mass number (*m/e* 176) were 22 and 31 %, respectively. The spectrum of the perchloric acid salt of the thiopyrylium betaine shows substantial pyrolytic dimerisation. The relative intensities vary somewhat in accordance with pyrolytic reactions. In a representative spectrum the base peak has the mass number of the betaine (*m/e* 176) while *m/e* 177 is 39 %

and the dimeric molecular ion (*m/e* 352) intensity 5 %. The data are consistent with competition between direct evaporation of a monomeric species and dimerisation before evaporation.

The dimeric structures can be regarded as 1,4-dithiane derivatives fixed rigidly in the boat or the chair conformation. The dihedral angle in the *syn*-isomer (boat conformation) is small. In the *anti*-isomer (chair conformation), however, the dihedral angle is probably not far from 60° and this isomer therefore has the less vicinal steric repulsion. The effect of the 1-methyl group is therefore to stabilise the incipient positive charge on C1, which is expected to increase the selectivity in the reaction of this species, as well as to increase the relative activation energy for the formation of the *syn*-isomer due to larger non-bonded interaction than in the *anti*-isomer. It is suggested that further substitution will favour *anti*-isomer formation when dimerisation occurs. The vicinal interaction in the dimer may be an important reason why 1,3-diphenyl derivatives do not dimerise in this way, but undergo 1,3-dipolar cycloadditions.

EXPERIMENTAL

The NMR spectra were recorded on a Varian A-60A or a Varian A-100 instrument, the UV spectra on a Cary 14 spectrophotometer and the mass spectra on an AEI-902 mass spectrometer.

4-Hydroxy-1-methyl-2-benzothiopyrylium perchlorate (2). 1-Methylisothiochroman-4-one (1.78 g, 0.01 mol) was dissolved in anhydrous acetonitrile (10 ml) and triphenylmethyl perchlorate (3.42 g, 0.01 mol) added. The reaction medium was heated at 60 °C for 10 min, left to cool and poured into anhydrous ether (200 ml) The precipitated greenish perchlorate was recrystallised from acetic acid; yield 1.90 g (70 %), m.p. 160–161 °C (decomp.) (Found: C 43.45; H 3.13. Calc. for $C_{10}H_8OS.HClO_4$: C 43.40; H 3.28); $\delta(CD_3CN)$ 3.4 (Me), 8.0–8.3 (H-arom); λ_{max} (MeCN) 228 (log ε 4.12), 258 (4.26), 293 (3.34), 312 (3.33), 324 (3.10), and 392 nm (3.81).

anti-*5,12-Dimethyl-5,6,12,13-tetrahydro-5,13:-6,12-bisepithiodibenzo*[a,f]*cyclodecene-7,14-dione (4).* 4-Hydroxy-1-methyl-2-benzothiopyrylium perchlorate (2.76 g, 0.01 mol) was dissolved in anhydrous THF (200 ml) and a solution of triethylamine (1.01 g, 0.01 mol) in anhydrous THF (50 ml) added dropwise over 1 h with stirring at room temperature. The solution was coloured deeper yellowish-green during the triethylamine addition and the colour disappeared when the reaction was completed. The solution was then washed with water, dried and evaporated. The residual material was dissolved in methylene chloride and the solution chromatographed on silica gel (0.2–0.5 mm). The material eluted with methylene chloride was recrystallized from chloroform; yield 1.23 g (70 %), m.p. 276–277 °C. (Found: C 67.99; H 4.37. Calc. for $C_{20}H_{16}O_2S_2$: C 68.17; H 4.55); δ(DMSO-d_6) 1.5 (s, Me-5, Me-12) 4.0 (s, H-6, H-13), 7.5–7.7 (6*H*-Ph), and 7.9–8.3 (2H-Ph *peri* to CO); λ_{max} (MeCN) 230 (log ε 4.30), 249 (4.32), 301 (3.55), 360 (2.37), 378 (2.82), and 395 nm (2.72); λ_{max} (KBr) 1650 cm^{-1} (CO); *m/e* (m.s.) 352 (22 %, M), 319 (19), 208 (18), 177 (100), 176 (31), 148 (20), and 147 (24).

REFERENCES

1. Baklien, S., Groth, P. and Undheim, K. *J. Chem. Soc. Perkin Trans. 1* (1975) 2099.
2. Katritzky, A. R. and Takeuchi, Y. *J. Chem. Soc. C* (1971) 874.
3. Denis, N., Katritzky, A. R. and Takeuchi, Y. *J. Chem. Soc. Perkin Trans. 1* (1972) 2054.
4. Undheim, K. and Baklien, S. *J. Chem. Soc. Perkin Trans. 1* (1975) 1366.
5. Nilsen, B. P. and Undheim, K. *Acta Chem. Scand. B. In press.*
6. Lown, J. W. and Matsumoto, K. *Can. J. Chem. 49* (1971) 3446.
7. Zimmerman, H. E. and Simkin, R. D. *Tetrahedron Lett.* (1964) 1847.
8. Groth, P. *Acta Chem. Scand. A 29* (1975) 298.
9. Cagniant, P., Jecko, G. and Cagniant, D. *Bull. Soc. Chim. Fr.* (1961) 2231.
10. Price, C. C., Hori, M., Parasaran, T. and Polk, M. *J. Amer. Chem. Soc. 85* (1963) 2278.
11. Pulman, D. A. and Whiting, D. A. *J. Chem. Soc. Perkin Trans 1* (1973) 410.

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