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TANDEM REACTIONS IN THE IODINATION OF 2-(2-BROMOALLYL)THIOQUINOLINE

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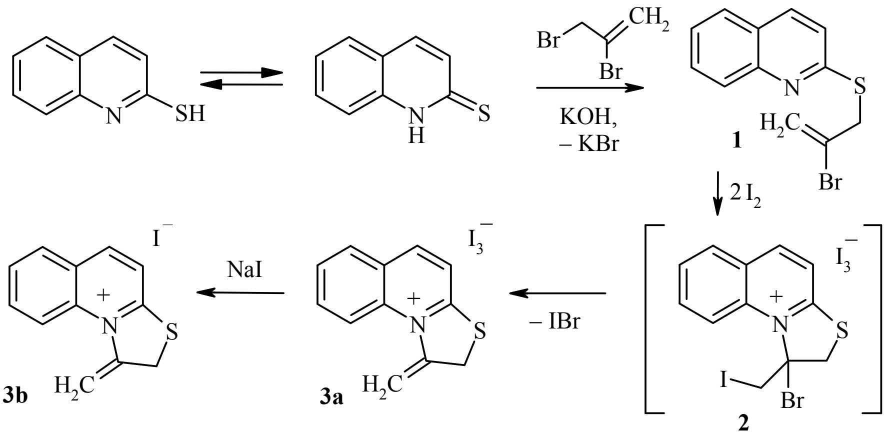
It is known that 2-allylthioquinoline reacts with iodine to form 3-iodomethyl-2,3-dihydro[1,3]thiazolo-[3,2-*a*]quinolinium iodides [1]. In this work we have studied the iodination of 2-(2-bromoallyl)thioquinoline (**1**) which was prepared by the reaction of 2-quinolinethione with 2,3-dibromo-1-propene in 2-propanol in the presence of alkali.



The theoretical reaction of iodine with compound **1**, as with 2-allylthioquinoline, can occur *via* an iodocyclization reaction to give the 1-bromo-1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium triiodide (**2**). Using X-ray structural analysis we have shown that the reaction product is 1-methylidene-1,2-dihydro-[1,3]thiazolo[3,2-*a*]quinolinium triiodide (**3a**) which is evidently formed as the result of the splitting off iodine bromide from compound **2**. According to this X-ray structural analysis, compound **3a** (see Figure 1) is crystallized

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in centrosymmetric space group symmetry. The quinoline ring is almost planar, the dihydrothiazole ring being found in a *pseudo envelope* conformation. The C(10) atom deviates from the mean square C(2)N(1)C(3)S(2) plane by 0.533 Å and the C(7) atom by 0.674 Å. The bond length for C(2)=C(7) is 1.308(7) Å and is typical for a conjugated C=C bond.

The triiodide **3a** is converted by the reaction with NaI in acetone to the monoiodide **3b**. The ^{1}H NMR spectrum of compound **3b** shows signals for the SCH_2 and $=CH_2$ group at 4.67 and 6.18 ppm respectively. The signals for the protons of the quinoline ring are shifted to lower field when compared with the spectrum of compound **1**.

^{1}H NMR spectra were recorded on a Bruker DRX-400 instrument (400 MHz) using DMSO-d_6 with TMS as internal standard. Mass spectra (EI, 70 eV) were taken on a Agilent Technologies GC-MS computerized system with a 6890N gas chromatograph and a 5975 mass selective detector.

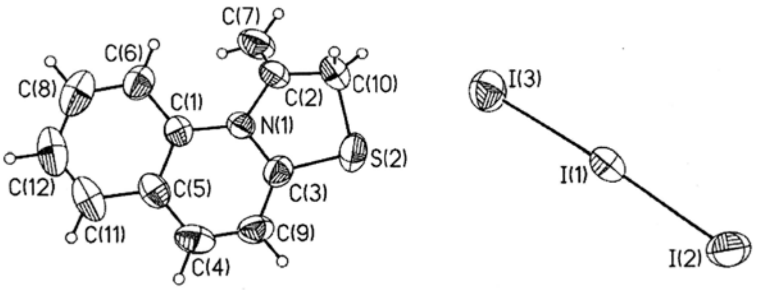

Fig. 1. General view of compound **3a** from the X-ray analysis with 50% probability thermal ellipsoids.

The X-ray structural analysis of compound **3a** was carried out on an automatic, four circle Xcalibur 3 X-ray analyzer using a standard procedure (MoKα radiation, graphite monochromator, 295(2) K, ω/2θ scanning). A fragment of the brown crystal plate of size 0.228×0.074×0.008 mm was used for the analysis. The crystal is triclinic with space group *P*-1 and unit cell parameters $a = 8.0011(3)$, $b = 9.8701(3)$, $c = 11.4349(3)$ Å, $\alpha = 80.619(3)^\circ$, $\beta = 70.998(4)^\circ$, $\gamma = 67.398(4)^\circ$, $V = 787.51(4)$ Å^3, for the empirical formula $C_{12}H_{10}I_3NS$: $Z = 2$, $d_{calc} = 2.450$ g/cm^3, $\mu = 6.066$ mm^{-1}. 4551 Reflection were collected in the range $2.95 < \theta < 28.28^\circ$ of which 3770 were independent ($R_{int} = 0.0124$) including 2643 with $I > 2\sigma(I)$, for $\theta = 26.00^\circ$ the completeness was 97.5%. Corrections for absorption were made analytically [2] using the polyhedral crystal model. The structure was solved and refined using the *SHELX* [3] program package. All of the non-hydrogen atoms were refined in the anisotropic approximation, hydrogen atoms were included in the geometrically calculated positions and included in the refinement using the "riding" model with related isotropic thermal parameters. The final refinement structural parameters were: $R_1 = 0.0313$, $wR_2 = 0.0942$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0481$, $wR_2 = 0.0994$ (for all reflections) with a quality S factor of 1.003. Peak maxima and minima for the residual electron density were $\Delta\rho = 0.928$ and -1.320 e/Å^3.

The crystallographic information has been placed in the Cambridge Structural Database as deposit CCDC 793710.

2-(2-Bromoallyl)thioquinoline (1) was prepared using method [1] as an oil, readily soluble in ether and chloroform. Yield 0.245 g (88%). ^{1}H NMR spectrum, δ, ppm (J, Hz): 4.47 (2H, s, SCH_2); 5.59 (1H, s, CH_2=); 6.12 (1H, s, CH_2=); 7.44 (1H, d, J = 8.64, H-3); 7.53, 7.74, 7.91 (4H, m, benzene ring); 8.21 (1H, d, J = 8.64, H-4). Mass spectrum, m/z (I_{rel}, %): 281 $[M+1]^+$ (1), 200 $[M-80]^+$ (100), 161 $[M-119]^+$ (15) etc.

1-Methylidene-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium Triiodide (3a). A solution of iodine (0.051 g, 0.2 mmol) in glacial acetic acid (5 ml) was added to a solution of sulfide **1** (0.028 g, 0.1 mmol) in glacial acetic acid (3 ml). The precipitated black solid was dissolved in acetone and reprecipitated using ether. Yield 0.064 g (81%); mp 88°C (decomp.).

1-Methylidene-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium Iodide (3b). NaI was added to a solution of compound **3a** in acetone. The precipitated yellow solid was filtered off. Mp 173ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.67 (2H, s, H-2); 6.16 and 6.20 (2H, two s, $=CH_2$); 8.27 (1H, d, *J* =8.91, H-4); 8.95 (1H, d, *J* = 8.91, H-5); 7.90, 8.12, 8.36, 8.56 (4H, benzene ring).

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