# A Stable Thio-analogue of a Meisenheimer Complex *via* a Spiroannelation Route: Requirements for Annelating Chain Length

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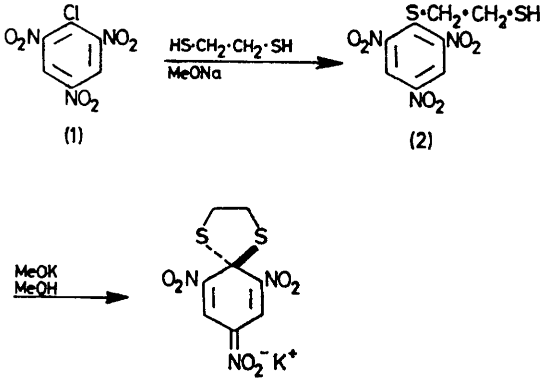
*Summary* 2-Picrylthioethane-1-thiol undergoes exclusive intramolecular cyclization to give a crystalline spiro thio-analogue of a Meisenheimer complex under the action of a base, whereas nitro group replacement by thiolate occurs with the propanedithiol analogue.

In contrast with Meisenheimer complexes,[1] which have been isolated as the *gem*-form,[2] their thio-analogues have only been observed in solution as ephemeral species because of rapid replacement of nitro groups by thiolates, the *gem*-form, moreover, being thermodynamically disfavoured with respect to the isomeric 1,3-type adduct.[3]

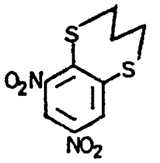
We report the formation of the *gem*-type adduct in a stable (spiro) form, *via* a spiroannelation route, the length of the annelating chain being critical.



(1) (2)

(3)

Thus, reaction of picryl chloride (**1**) with one molar equivalent of both ethane-1,2-dithiol and sodium methoxide in methanol afforded (**2**).[4] Treatment of (**2**) with one molar equivalent of potassium methoxide in methanol followed by the addition of toluene gave (**3**) as an amorphous red powder in high yield,[4] whilst addition of a little toluene and cooling to −20° gave (**3**) as red crystals m.p. 157° (decomp.); $\delta$ [$(CD_3)_2CO$, $Me_4Si$] 3·84 (4H, s), 8·40 (2H, s); $\lambda_{max}$ ($Me_2SO$) 454, 534, 564 nm, similar to non-spiro thio-analogues of Meisenheimer complexes;[3] $\nu_{max}$ 1390, 1225 ($NO_2$) (the low frequency can be attributed to negative charge acceptance.[5]) $^2H$ n.m.r. shows that (**3**) is the only stable compound formed.



(4)

When propane-1,3-dithiol was used in the place of ethane-1,2-dithiol only compound (**4**), m.p. 175°, was so far isolated in low yield,[4] $^1H$ n.m.r. and u.v. spectroscopy revealed that Meisenheimer complexes occurred as unstable intermediates. Possibly steric interference of the 1,3-dithione unit with the *ortho*-nitro-group in the propane-1,3-dithiol analogue of (**3**) is responsible for such instability.

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[4] All new products, which analysed correctly, gave single spots in t.l.c., their structures being fully supported by n.m.r., i.r., u.v., and m.s. data.

[5] L. K. Dyall, *J. Chem. Soc.*, 1960, 5160.

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