Tetrahedron Letters No. 24, pp 2137 - 2138, 1978.
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0040-4039/78/0608-2137$02.00/0

A FACILE 1,2-ANNELATION OF CYCLOHEPTATRIENONE WITH DITHIOLS. FAILURE OF A DITHIOKETALIZATION

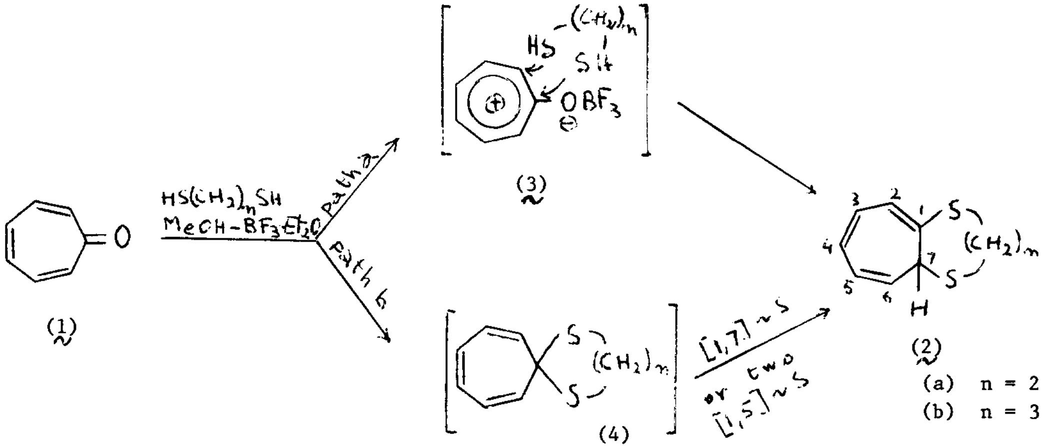
Marino Cavazza and Gioia Morganti
(Istituto di Chimica Generale, Università di Pisa, 56100 Pisa),
and Francesco Pietra
(Facoltà di Scienze, Libera Università di Trento, 38050 Povo-Trento, Italy)

(Received in UK 10 April 1978; accepted for publication 18 April 1978)

We report that treatment of cycloheptatrienone with either 1,2-ethanedithiol or 1,3-propanedithiol at room temperature, under typical conditions for dithioketalization of ketones,[1] resulted instead in a fast 1,2-annelation of dithiols to the polyenone.

Thus, to cycloheptatrienone (1) (1g; 9.4 mmol) in 70 ml of methanol was added, under N_2 with stirring, 1,2-ethanedithiol (1.4 ml). The mixture was stirred for 16 h under N_2, whereby it became yellow coloured with separation of a viscous oil which was washed with methanol. All the methanol phase was evaporated at r.t. at reduced pressure, the oily residue was taken with chloroform, washed with 5% $NaHCO_3$, dried over Na_2SO_4, and then evaporated at r.t. at reduced pressure to give 0.90 g of a pale-yellow oil. Half of this material was purified by preparative tlc (silica gel 2 mm; eluent hexane-ether 85 : 15; major band at R_F 0.6 plus very minor impurities) to give 0.4 g of (2a)[†] (M^+ 182; $\delta_{TMS}(CDCl_3)$ 2.5-3.5 (5H, complex m, for H (7) and the two non equivalent CH_2), 5.3 (1H, dd, J = 10 and 7 Hz, for H(6), and 6.1-6.6 p.p.m. (4H, complex m, for H(2) - H(5)). The identical material, in about the same yield, was arrived at by distillation of the remaining crude oil, 0.45g, (b.p. 74-75°, 0.065 mm Hg). Repetition of the reaction with tlc monitoring, only revealed the presence of (2a) at any time.

Reaction of (1) with 1,3-propanedithiol was run similarly. However, much tarry material separated out and, correspondingly, the yield of (2b),[†] the structure of which is also supported by both mass and m.m.r. spectral data, was lower than above (30%). No trace of the



Scheme 1

dithioketal was ever found even in this case.

We envisage two likely routes to the 1,2-annelated products (Scheme 1). Path a involves nucleophilic addition of sulphur at C(2) followed by intramolecular substitution at C(1) on the tropenylium-like adduct (3).

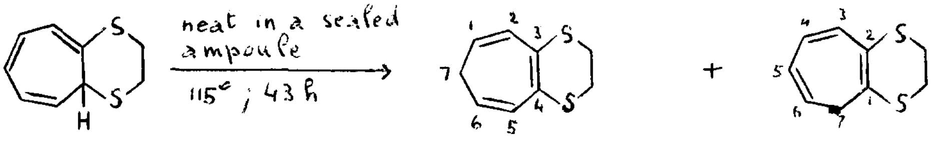
Path b involves the dithioketals (4) as labile intermediates which are rapidly rearranged at room temperature into (2) via either two consecutive [1,5]sigmatropic sulphur migrations or a [1,7] sigmatropic sulphur migration.

Whichever route is correct, formation of (2) is unusually interesting. Path a suggests the investigation of new annelating reactions with troponoids, whilst path b has broader implications, suggesting the exploitation, for synthetic problems, of the presumed extremely high aptitude of bicoordinated sulphur towards sigmatropic migrations.

Scheme 2

Such extremely high aptitude of sulphur to migrate is implicated (i) by the above results when compared with the report[2] that with oxygen in the place of sulphur (Scheme 2) rearrangements of the type at Scheme 1, path b, require drastic conditions, giving also much benzene and ethylene and (ii) by the observation that even with our system (2a) sigmatropic shifts of hydrogen only occur under usual, drastic conditions to give a ca. 1:1 mixture of (5) and (6)‡ (Scheme 3).

We acknowledge financial support from C.N.R., Roma.



(2a) (5) (6)

Scheme 3

REFERENCES AND FOOTNOTES

† Correct elemental analysis was obtained for all new products.

‡ Correct elemental analysis; the ^1H n.m.r. spectrum consisted of two equally intense series of signals attributable as follows. For (5) δ_{TMS} ($CDCl_3$) 2.3 (2H, t, J = 6 Hz, for $C(7)H_2$), 6.0 (2H, d, J = 8 Hz, for H(2) and H(5); for (6) 2.6 (2H, d, J = 7Hz, for $C(7)H_2$), 6.3 (2H, sharp m, for two of the olefinic protons), whilst the other two olefinic protons of (6) give a complex multiplet at 5.5 p.p.m. for 4H together with H(1) and H(6) of (5), and all sulphur-bound methylenes give a singlet for 8H at 3.1 p.p.m. The assignment is supported by irradiation at either 2.3 or 2.6 p.p.m. whereby the signal at 5.5 p.p.m. changes as expected. Also, on irradiation at 5.5 p.p.m. the doublet at 2.6 p.p.m. changes into a singlet.

1) M. Fieser and L.F. Fieser, "Reagents for Organic Chemistry" vol 5, p 290, Wiley-Interscience, 1975.

2) T. Fukanaga, T. Mukai, H. Akasaki, and R. Suzuki, Tetrahedron Lett. , 2975, 1970.