

Reaction of Acetylenic β -Diketones with Sodium Sulphide

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Summary: 1,5-Diarylpent-1-yne-3,5-diones (1) reacted with sodium sulphide in 60% dioxane-water mixture at 15° or fusion at 160-170° to give a mixture of the corresponding 2,6-diaryl-4-pyrones (2), 4-thiones (3) and 5-aryl-2-benzylidene-3(2H)-thiophenethiones (4). The structure of the above compounds was confirmed from their spectral characteristics. The mechanisms for these transformations are discussed.

Introduction

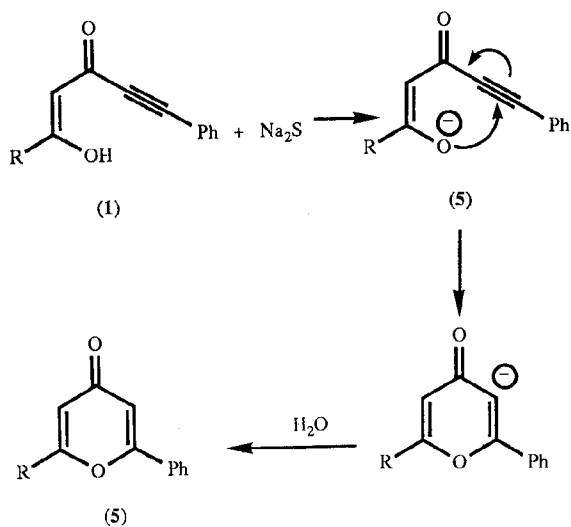
The literature on monoacetylenic ketones is fairly extensive. Attack on the triple bond or at the ketone function by a variety of reagents has been reported leading to useful cyclics [1]. By comparison, the synthetic applications of acetylenic β -diketones are largely very limited due to the difficulties encountered in their syntheses and their sensitivity toward heat [2,3] as well as acids [4,5]. However, in earlier publications [4,5-10], we reported some reactions of 1,5-diarylpent-1-yne-3,5-diones (1). In any case, any new information that

may be expected in the general area of alkyndiones should presumably derive from the presence of the second carbonyl group. No reports on the reaction of sulphur reagents with acetylenic β -diketones have been made earlier except the study of the reaction with phosphorous pentasulphide [10].

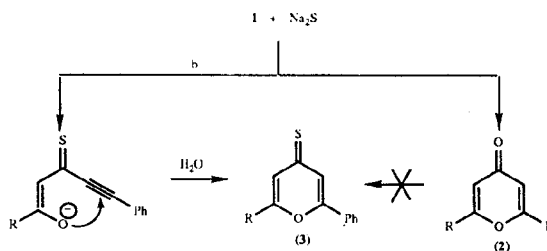
While aroylphenylacetylenes readily react with sodium sulphide in 60% dioxane-water mixture at 15° giving β -hydroxy- α -thiobenzoylstyrene derivatives [11], the acetylenic β -diketones (1a-e)

afforded under the same conditions 2,6-diaryl-4H-pyran-4-ones (2a-e), 4-thiones (3a-e) and 5-aryl-2-benzylidene-3(2H)-thiophenethiones (4a-e). The same products were also formed when 1 and sodium sulphide were heated at 160-170° for 10-15 minutes.

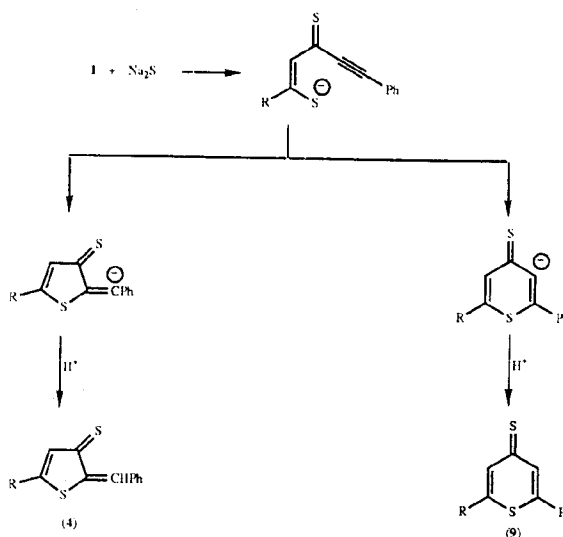
The formation of the pyrones (2) in the above reaction is assumed to proceed by initial formation of the anion 5 and subsequent cyclization (Michael type addition). This mechanism is supported by the fact that the acetylenic β -diketones are also converted into the 4-pyrones (2) by sodium ethoxide. Also, symmetrical diacetylenic ketones undergo similar reaction [12]. It is worthy to mention that the absence of furanones (7) in the above reactions may be due to the strongly basic conditions which would minimize the concentration of the species containing chalcogen-hydrogen bonds, which are believed to be necessary for the anti-Michael addition [13,14].



4-Thiopyrones (3) are assumed to be formed either by initial cyclization of 1 into the pyrones (2) followed by thionation (route a) or by initial thionation of the carbonyl (position-3) and subsequent cyclization (route b). Since 2,6-diaryl-4H-pyran-4-ones (2) were recovered unchanged on treatment with sodium sulphide in 60% dioxane-water mixture, route a may be excluded under these conditions. Conversion of 2 into 3 under fusion conditions was tested, only traces of 3 were formed and the major product was 2.



The formation of 5-aryl-2-benzylidene-3(2H)-thiophenethiones (4) from the reaction of acetylenic β -diketones and sodium sulphide in 60% dioxane-water mixture is assumed to proceed by initial thionation giving the anion 8 followed by anti-Michael type of addition. In accordance with Baldwin rules for ring closure [15], this type of cyclization, 5-exo-digonal for the thiophenethiones (4) is more favourable due to spacial requirements which appear to make the acetylenic carbon α to the thiocarbonyl group more accessible to the nucleophilic attack by sulphur and also due to the ability of sulphur to form 5-membered ring rather than 6-membered ring. Since no 4H-thiopyran-4-thiones (9) were detected in the above reaction a Michael type of addition can be excluded.

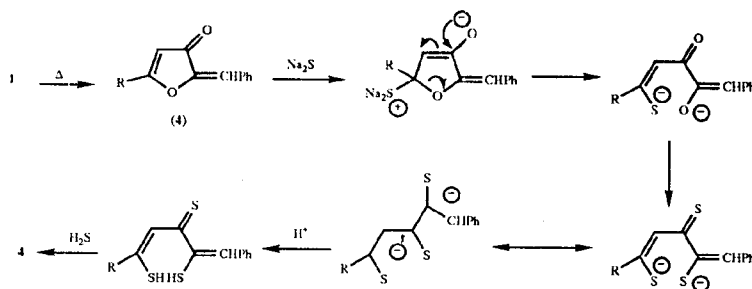


It is worthy to mention that similar anti-Michael mechanisms were suggested for the formation of thiocyclopentenone [16], selenocyclopentenone [17] and 2,3-dihydrotellurophene [14] from the reaction of 1,5-diphenylpentadiyn-3-one with thiourea, hydrogen selenide and bis (tert-butyl-

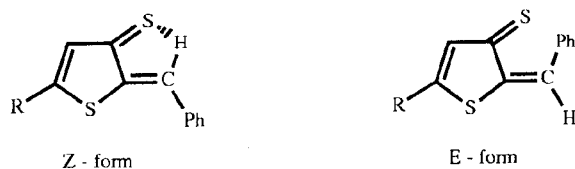
dimethylsilyl) telluride, respectively and also for pyrrolinones [16] from the amine adducts of pentadiyn-3-ones.

While the 3(2H)-furanones (7) were recovered unchanged after treatment with sodium sulphide in 60% dioxane-water, they were converted into the corresponding thiophenethiones (4) when heated at 160-170°. This suggests that the formation of 4 by heating acetylenic β -diketones and sodium sulphide may involve initial formation of the furanones (7) followed by Michael addition of sodium sulphide at C-5, ring opening to the resonance-stabilized anion 10 and subsequent cyclization. It is worthy to mention that ring opening of furanones with nucleophile such as hydrazines [2,18-20], amines [21] and alkalis [22] has been reported.

Alternatively, the possible intermediacy of (7) does not exclude that (4) may be also formed via (8).



The infrared spectra of 4 exhibited the thiocarbonyl absorption in the region 1100-1122 cm^{-1} [23] (Table 1). E and Z isomerism is possible in the case of benzylidenethiophene-thiones. Similar to 2-benzylidene-5-aryl-3(2H)-furanones [2], the z-configuration is tentatively assigned for these compounds, since it is expected to be more favoured due to intramolecular hydrogen bonding.



Also $^1\text{H-NMR}$ studies of stereoisomerism of some 3-aryldenebutenolides, 4-arylidenoaxolin- and indazolin-5-ones showed that structures in which the

aryl nucleus is more remote from the endocyclic carbonyl group are favoured [24]. It is worthy to mention that no appropriate $^1\text{H-NMR}$ data could be obtained for the thiophenethiones (4) due to the difficulties encountered in their solubility.

The structure of 3(2H)-thiophenethiones (4) was further confirmed from their mass spectra. The fragmentation pattern of 2-benzylidene-5-p-methylphenyl-3(2H)-thiophenethione was generally similar to that of 5-aryl-2-benzylidene-3(2H)-furanones [2]. The loss of sulphur from the molecular ion to give the species at m/z 262 ($\text{C}_{18}\text{H}_{14}\text{S}$) has been contrasted with the absence of direct losses heteroatom from comparable furans and pyrroles [25].

Experimental

Microanalyses were performed by the Microanalysis Unit Cairo University, Cairo. IR spectra were recorded in KBr on a Unicam SP 1025

spectrophotometer (ν_{max} in cm^{-1}). Mass spectra were recorded on an AEI MS 30 spectrometer. When compounds are stated to be identical, their identity has been established by comparison of m.p., mixed m.p., I.R. and $^1\text{H-NMR}$ data.

Reaction of acetylenic β -diketones with sodium sulphide (Table)

A solution of sodium sulphide (0.4 g; 0.0017 mol) in 60:40 dioxane-water mixture (15 ml) was added to a stirred solution of acetylenic β -diketones (1a-e) (0.5 g; 0.0020 mol) in the same solvent (10 ml) at room temperature and allowed to stand with stirring for 5 hr. The reaction mixture was then poured into cold water and the precipitated solid was filtered, washed with water, dried, dissolved in ethanol and treated with saturated ethanolic solution of picric acid. The separated picrate was crys-

Table 1: Analytical data and IR of the 3(2H)-thiophenethiones (4)

Compd.	m.p. °C	Formula	Found (%) (Calc.)				IR (cm ⁻¹) νC=S
			C	H	X	S	
4a	115	C ₁₇ H ₁₂ S ₂	72.7 (72.9)	4.4 4.3	-	23.0 22.9	1100
4b	115	C ₁₈ H ₁₄ S ₂	73.4 (73.5)	4.9 4.8	-	21.7 21.8	1105
4c	117	C ₁₈ H ₁₄ OS ₂	69.9 (69.7)	4.6 4.5	-	20.9 20.7	1100
4d	113	C ₁₇ G ₁₁ BrS ₂	56.6 (56.8)	3.0 3.1	22.0 22.3	17.7 17.8	1110
4e	118	C ₁₇ H ₁₁ ClS ₂	65.0 (64.9)	3.4 3.5	11.5 11.3	20.3 20.4	1122

	R
a,	C ₆ H ₅
b,	p-Me-C ₆ H ₄
c,	p-MeO-C ₆ H ₄
d,	p-Br-C ₆ H ₄
e,	p-Cl-C ₆ H ₄

tallized from ethanol and hydrolysed with 25% aqueous ammonia to give the respective 4H-pyran-4-ones (2a-e) (18-20% yield).

The ethanolic solution left after separation of the 4-pyrone picrates was mixed with 25% aqueous ammonia, warmed, diluted with water and extracted with chloroform. The residue after evaporation of the solvent afforded the corresponding 4-thiones (3a-e) (55-65% yield) on treatment with petroleum ether (b.p. 60-80°) which were identical with authentic samples prepared from 2a-e and phosphorus pentasulphide [26].

The aqueous layer left after separation of 2 and 3 was acidified with 10% cold hydrochloric acid (30 ml). The thiophenethiones (4a-e) (20-25% yield) was filtered, washed with cold water, dried and crystallized from ethanol in pale yellow needles, 4b: m/z 294 (M⁺, 12), 293 (7), 263 (12), 262 (58), 261 (15), 260 (3), 250 (8), 235 (19), 234 (25), 202 (8), 134 (3), 119 (16), 118 (7), 117 (10), 116 (17), 115 (30), 102 (13), 91 (18), 90 (3), 89 (4), 78 (20), 77 (13), 63 (100), 32 (23).

The same products were also obtained when a mixture of 1a-e (0.5 g; 0.0020 mol) and sodium sulphide (0.33 g; 0.0014 mol) was heated on an oil-bath (160-170°) for 10-15 min.

Reaction of 3(2H)-furanones with sodium sulphide

A mixture of 2-aryl-5-benzylidene-3(2H)-furanone [2] (7a-e) (0.3 g; 0.0012 mol) and sodium

sulphide (0.3 g; 0.0013 mol) was heated on an oil-bath (160-170°) for 10-15 min. The residual solid on treatment with cold water and then acidification with 10% hydrochloric acid gave the 3(2H)-thiophenethiones (4a-e) (22-28% yield) after filtration, washing, drying and crystallization from ethanol.

Action of sodium ethoxide on the acetylenic β-diketones

A suspension of (1a-e) (0.5 g; 0.0020 mol) in ethanol (12 ml) was kept at room temperature with sodium ethoxide (0.3 g; 0.0044 mol) overnight with frequent shaking. The reaction mixture was poured into water and the separated 4H-pyran-4-ones (2a-e) (70-80% yield) were crystallized from methanol.

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