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PHOTOADDITION OF NON-CISOID 1,2-DIKETONES(1) AND PHENYLGLYOXAL(1) TO ALKYLTHIOACETYLENES(2); PREPARATION OF 3-ALKYLTHIOFURANS(5)

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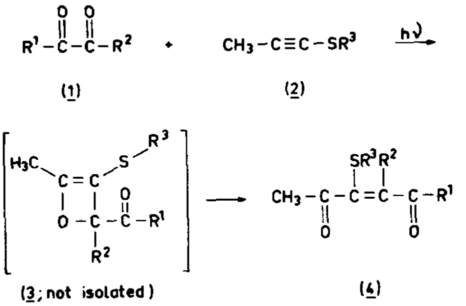
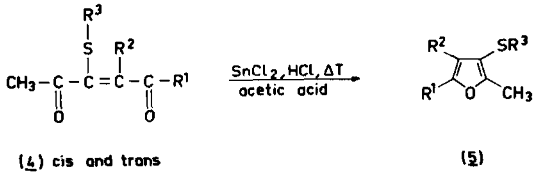
Photoaddition of phenanthraquinone to alkoxyacetylenes affords 1,4-adducts: dihydrodioxins or dioxoles[1]. The non-cisoid 1,2-dioxo compounds give with alkenes 1,2-cycloaddition[2] under formation of α-keto-oxetanes. Irradiation of the non-cisoid 1,2-dioxo compounds benzil, biacetyl, 1-phenylpropan-1,2-dione and phenylglyoxal (1: $R^1=R^2=C_6H_5$, $R^1=R^2=Me$, $R^1=C_6H_5$ $R^2=CH_3$, and $R^1=C_6H_5$ $R^2=H$ respectively) with 1-alkylthio-1-propynes (2: R^3=Me, Et, *t*-Bu, and C_6H_5) in benzene through G.W.V.glass[3] gives rise to *cis* and *trans* 2-alkylthio-2-buten-1,4-diones (4) in yields up to 45%. These adducts (4) are undoubtedly formed, via an oxete derivative (3), through 1,2-cycloaddition of one oxo group of (1) to the triple bond. *Cf.*[4,5].



These adducts are useful starting materials for the preparation of 3-alkylthiosubstituted furans. It is possible to convert in good yield 2-alkylthio-2-buten-1,4-diones with $SnCl_2$, acetic acid and some hydrochloric acid in tri- and tetrasubstituted furans (5). *Cf.*[6].



The 2-alkylthio-2-buten-1,4-diones and the furans were isolated by chromatography and identified by ^1H-NMR, IR, UV and MS. The mass spectra of the furans showed amongst others important peaks at m/e= P(arent), P minus R^1CO and P minus CH_3CO;for R^3= t-C_4H_9, P minus C_4H_8 is very strong.

Compounds (4) and (5) prepared

R^1	R^2	R^3	Yield (4) (%)	Yield (5) (%)	MS (5); strongest peaks (m/e)
Ph	Ph	*t*-Bu	45	90*	322, 266, 105, 43
Ph	H	Me	20	90	204, 189, 105, 43
Ph	H	Et	20	80	218, 189, 105, 43
Ph	H	*t*-Bu	25	90	246, 190, 105, 43
Ph	H	Ph	25	95	266, 189, 105, 43
Me	Me	*t*-Bu	20	95	198, 142
Ph	Me	*t*-Bu	10**	85	260, 204, 105, 43
Me	Ph	*t*-Bu		85	260, 204, 43

* In this case only one isomer of (4) could so far be cyclized.
** Both compounds are formed from 1-phenyl-propan-1,2-dione.

Typical Experimental Procedure:

A solution of 2 g of phenylglyoxal (1: R^1=Ph, R^2=H) and 2 g of 1-*tert*-butylthio-1-propyne (2: R^3=t-Bu) was irradiated (Philips HPK-125W) in 500 ml of benzene under nitrogen, using G.W.V.glass[3] (transmission <1% at 360 nm) as a filter. After 2 h the solvent was evaporated and the residue was submitted to dry column chromatography (SiO_2/benzene). Yield 25% of (4: R^1=C_6H_5, R^2=H, R^3=t-Bu); ^{1}H-NMR in CCl_4: $\delta(C(CH_3)_3)$= 1.37, $\delta(CH_3)$= 2.28, $\delta(=CH)$= 6.80 ppm for the *cis* isomer and $\delta(C(CH_3)_3)$= 1.13, $\delta(CH_3)$= 2.36, $\delta(=CH)$= 7.14 ppm for the *trans* isomer[7]. A mixture of 2.2 g of (4: R^1=Ph, R^2=H, R^3=t-Bu and 8.0 g of $SnCl_2$, 5 ml of concentrated hydrochloric acid in 20 ml acetic acid was heated to 80° during 10 min. Yield 90% of (5); ^{1}H-NMR in CCl_4: $\delta(C(CH_3)_3)$= 1.20, $\delta(CH_3)$= 2.33, $\delta(=CH)$= 6.54 ppm. UV in hexane: maxima (nm) at 304(ε=1.1×10^4), 290(ε=1.7×10^4), 284(ε=1.6×10^4), 248(ε=0.5×10^4), 228(ε=0.7×10^4), 213(ε=1.1×10^4).

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