Tetrahedron Letters Vol. 21, pp 4085 - 4086
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/1015-4085$02.00/0

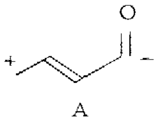
PREPARATION OF α-ETHYLENIC KETENE DITHIOACETALS FROM α-OXOKETENE DITHIOACETALS.

Serge Masson and André Thuillier*

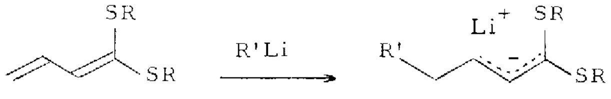
Laboratoire des Composés Thioorganiques (ERA 391), Université, 14032 CAEN, France.

Summary : 1,1-bis (methylthio)-1,3-dienes and 1,1-bis (methylthio)-3-trimethylsilyloxy-1,3-dienes were respectively prepared by Wittig olefination and by enol-silylation of α-oxoketene dithioacetals.

Conjugated ketene dithioacetals are synthetic reagents which can be used as diene components in Diels Alder reactions [1] and as the synthetic equivalent with "reactivity umpolung" A [2a,b].



A



B

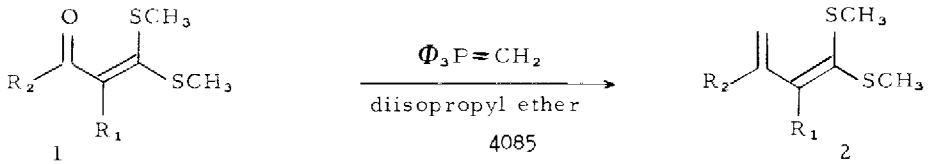
The conjugated addition of organolithium compounds to these dithioacetals produces conjugated acylanion equivalents such as B and the syntheses of (-) (E) - Lanceol[3] and of Manicone [4] have been realized by this process.

α- Ethylenic ketene dithioacetals have been previously prepared by the Peterson olefination of α-unsaturated ketones with 2-lithio-2-trimethylsilyl-1,3-dithiane [5a,b,c] or via one of the following processes recently described : a) 2,3 sigmatropic rearrangement of acetylenic sulfonium ylides [6], b) enethiolization and alkylation of β-ethylenic dithioesters [3,4] , c) 2,3 sigmatropic rearrangement of dithiocarbenes generated from tosylhydrazones of S-allylic dithiocarbonates.[7]

Besides, the synthetic interest in Diels Alder reactions of functionalized butadienes such as 1-methoxy- or 1,1-bis (methoxy)-3-trimethylsilyloxy-1,3-butadienes prepared by enol - sylilation of the corresponding ketones was recently demonstrated [8].

In this communication we show that sulfurated dienic synthons can be easily obtained from α-oxo-ketene dithioacetals[9] by a Wittig reaction or by an enol-silylation leading respectively to α-ethylenic dithioacetals or to O-silylated α-ethylenic dithioacetals :

Wittig olefination :



1

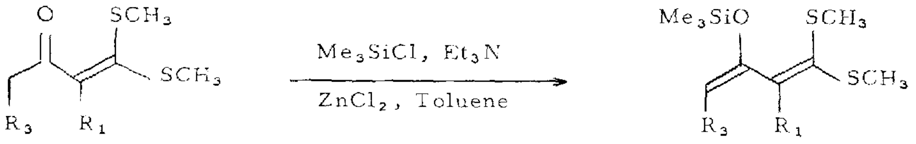
2

$\underline{1}$	R_1	R_2	$\underline{2}$ (yield %)	b.p/ 0.05 torr.
$\underline{1}$ a	H	CH_3	$\underline{2}$ a (80) [(a)]	50 °
$\underline{1}$ b	CH_3	CH_3	$\underline{2}$ b (84)	42°
$\underline{1}$ c	H	C_6H_5	$\underline{2}$ c (61)	(b)
$\underline{1}$ d	CH_2-CH_2-CH_2		$\underline{2}$ d (85)	86° [(b)]
$\underline{1}$ e	CH_2-$(CH_2)_2$-CH_2		$\underline{2}$ e (90)	107° [(b)]

a) THF used as solvent gave the same yield. b) These dithioacetals were purified by chromatography since they polymerize partially during distillation.

Typical procedure : to a cooled solution (~15°) of the Wittig reagent (prepared under nitrogen from 0.015 mole of triphenyl phosphonium bromide and 1 equiv. of tert-BuoK in 50 ml of refluxing diisopropyl ether) was added with stirring 0,01 mole of α-oxoketene dithioacetal and the mixture was stirred for 1 hr at room temperature. After dilution of the reaction mixture with 150 ml of light petroleum ether most of the triphenylphosphine oxide was eliminated by filtration. The filtrate was washed with dilute HCl, water, brine and the solvent was eliminated under vacuo. The residual oil was taken up with pentane, ice-cooled and filtered again. Pentane was evaporated and the crude product was purified by distillation or by passing through a column of silica (florisil).

Enol-silylation :



$\underline{1}$

$\underline{3}$

$\underline{1}$	R_1	R_3	$\underline{3}$ (yield %)	b.p. / 0.01 torr.
$\underline{1}$ a	H	H	$\underline{3}$ a (80)	81°
$\underline{1}$ b	CH_3	H	$\underline{3}$ b (74)	72°
$\underline{1}$ e	CH_2-CH_2-CH_2		$\underline{3}$ e (76)	107°

The procedure described for the preparation of 1-methoxy-2 methyl-3-trimethylsilyloxy-1,3-butadiene[8] was used. A much longer reaction time (8 days) was needed for the preparation of $\underline{3}$ b.

The structures of all the new compounds were readily deduced from NMR, IR and mass spectra. Synthetic applications of these dienes are now under investigation.

References

1) F.A. Carey and A.J. Court, J.Org.Chem., 37, 4474 (1972).
2) (a) D. Seebach, M. Kolb and B.T. Gröbel, Angew.Chem.Int.Ed. 12, 69 (1973) ; (b) B.T. Gröbel and D. Seebach, Synthesis, 357 (1977).
3) B. Cazes and S. Julia, Tetrahedron Lett., 4065 (1978).
4) P. Gosselin, S. Masson and A. Thuillier, C.R.Acad.Sci. in press.
5) (a) D. Seebach, M. Kolb and B.T. Gröbel, Chem.Ber., 106, 2277 (1973) ; (b) F.A. Carey and A.S. Court, J.Org.Chem., 37, 1926 (1972) ; (c) P.F. Jones and M.F. Lappert, J.Chem.Soc.Chem.Comm., 526 (1972).
6) V. Ratovelomanana and S. Julia Synth.Comm. 8, 87 (1978).
7) T. Nakai and K. Mikami, Chem.Lett. 1243 (1978).
8) S. Danishefsky, T. Kitahara, C.F. Yan and J. Morris, J.Amer.Chem.Soc. 101, 6996 (1979) and references of the following papers cited therein.
9) These compounds are readily prepared from ketones and carbon disulfide : a) A. Thuillier and J. Vialle, Bull.Soc.Chim. 1398 (1959) ; ibid. 2182 (1962) ; b) E.J. Corey and R. Chen, Tetrahedron Lett., 3817 (1973) ; c) T. Shahok and Y. Sasson, Tetrahedron Lett., 4207 (1973).

(Received in France 31 July 1980)