Tetrahedron Letters,Vol.24,No.44,pp 4829-4832,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain ©1983 Pergamon Press Ltd.

REACTIVITY OF THE 1-t.BUTYLTHIO-3-METHOXY-1-ALKENES TOWARDS METALATING AGENTS, II.

ALLYLIC DEPROTONATION OF THE E-ISOMERS AND OF THE Z-PROPENYL DERIVATIVE.

O. Ruel, C. Bibang Bi Ekogha, S.A. Julia *

E.R. 12 du C.N.R.S., Laboratoire de Chimie, Ecole Normale Supérieure,
24, rue Lhomond, 75231 Paris Cedex 05, France

Summary: Deprotonation of the title compounds with a lithiating agent and subsequent alkylation furnish the 1-substituted products 4. The 1-t.butylthio-3-methoxy-1-lithio-1-alkenes 3 become new equivalents of the hypothetical anions I.

In the course of our study of the title Z-compounds [1], the t.butylthio substituent of the propenyl derivative 1 [2] was expected not only to facilitate the allylic deprotonation 1 → 3 (R^1=H) [3], but particularly to direct the alkylation of 3 entirely towards the desired products 4 [4]. Indeed, treatment of 1 in THF at -78° (i) with 1.1 equiv of sec.butyllithium or (ii) with 10 mole % of diisopropylamine and 1.1 equiv of n.butyllithium [5] or (iii) with 1.1 equiv of lithium diisopropyl amide (LDA), followed by addition of alkyl halides, furnished regioselectively the 1-alkylated products 4 (E ± Z). The results are summarised in the table and the following features are noteworthy:

- the conditions (i) and (ii) gave better and more reproducible results than (iii);
- the kinetic lithio derivative is 3 (E, R^1=H) which is formed from the two favored conformations (1 A or B), since the major kinetic products are the E-compounds 4 R^1=H;
- upon standing at -78° during 90 min or at -25° for 1h, the E-lithio derivative isomerises to the Z-lithio derivative 3 (R^1=H) which may be stabilised by coordination of the lithium with a lone pair of the oxygen atom [6]. Subsequent alkylation yields mainly the Z-compounds 4 (R^1=H).

The E-propenyl derivative (2a, R^1=H) [2] was obtained from the 1-t.butylthio-1(Z)-propen-3-ol by treatment with methanesulfonyl chloride and triethylamine at -40° in CH_2Cl_2, followed by in situ methanolysis (50%) [7]. After treatment with LDA (conditions iii) followed by alkylation, it gave regularly the pure enol ethers 4 (Z, R^1=H) [2].

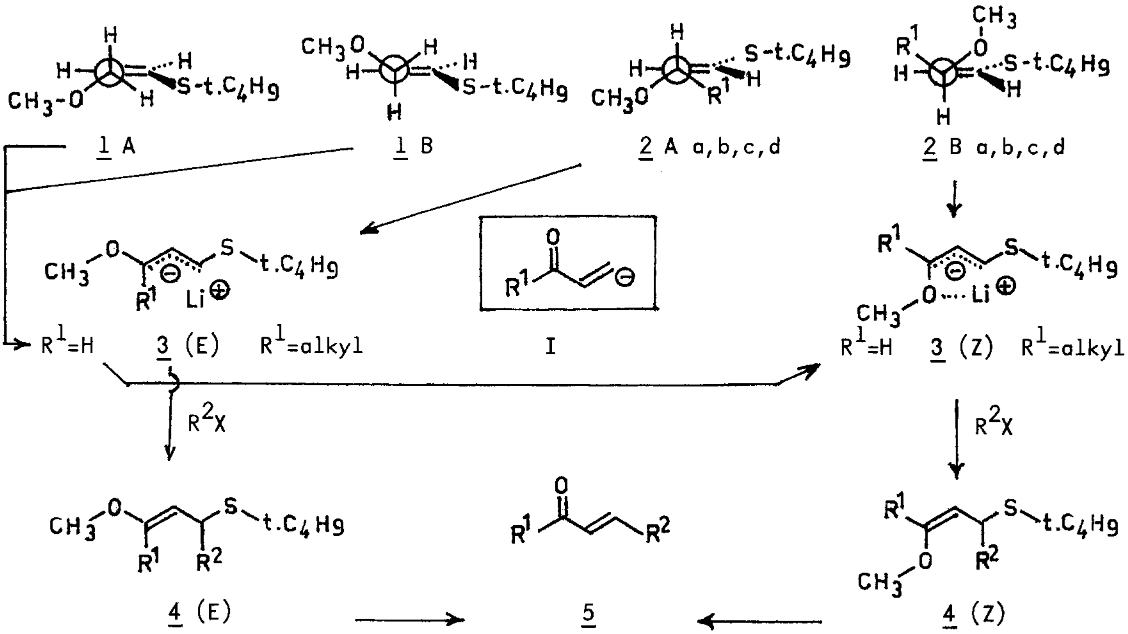
Table

Substrate	Conditions	R^2X	Products 4		Carbonyl compounds 5	
			yield % *	(E/Z) ratio	procedure	yield % *
1	(i) -78° 90 min	$(CH_3)_2C{=}CH{-}(CH_2)_2Br$	73	80:20	(iv)	64
	-78° 90 min	n.$C_6H_{13}Br$	94	85:15		
	-78° 90 min then -25° 60 min	n. $C_6H_{13}Br$	90	0:100		
	(ii) -78° 30 min	$C_6H_5{-}(CH_2)_3Br$	93	84:16	(iv)	65
	-78° 30 min	n.$C_6H_{13}Br$	85	88:12	(iv)	72
	-78° 30 min then -25° 60 min	n.$C_6H_{13}Br$	86	0:100		
	(iii) -78° 35 min	n.C_4H_9I	(91)	70:30	(iv)	42
	40 min	n.$C_7H_{15}Br$	(97)	70:30	(iv)	57
	120 min	n.$C_7H_{15}Br$	(98)	20:80		
2a R^1=H	(iii) -78° 30 min	CH_3I	71	0:100		
	110 min	n.C_4H_9I	(97)	0:100		
	45 min	n. $C_7H_{15}Br$	(96)	0:100	(iv)	69
2b R^1=CH_3	(i) -78° 45 min	CH_3I	83	28:72		
	60 min	n.C_4H_9I	80	40:60	(v)	55
	60 min	$(CH_3)_3SiCl$	92	27:73		
2c R^1=n.C_3H_7	30 min	CH_3I	(97)	13:87	(v)	64
	35 min	n.C_4H_9I	(75)	18:82	(v)	65
	30 min	$C_6H_5{-}CH_2Br$	(89)	26:74	(v)	57
	60 min	$(CH_3)_3SiCl$	87	17:83	(vi)	46
2d R^1=n.C_5H_{11}	60 min	CH_3I	93	15:85	(v)	58
	60 min	$(CH_3)_3SiCl$	(95)	20:80	(vi)	52

* The values in brackets are the yields of crude products whose purity is ensured by spectral data.

(i), (ii), (iii), (iv), (v), (vi): see the text

Reactions of the 1-t.butylthio-1(Z)-alken-3-ols with trimethyl orthoformate and 10 mole % trifluoroacetic acid at 0° furnished readily the pure methoxy-(E)-isomers (2b,c,d) (65-78 % yield) [2,7]. Treatment of (2,b,c,d) with sec.butyllithium followed by addition of alkyl halides gave the 1-alkylated products 4 in good yields [8]; as indicated in the table, the Z-isomers were always predominant [9].



	a	b	c	d
R^1	H	CH_3	$n.C_3H_7$	$n.C_5H_{11}$

The compounds (4, R^1=H) were smoothly hydrolysed using cupric chloride-cupric oxide in wet acetone [10] at room temperature (iv) to yield the trans α,β-unsaturated aldehydes (5 R^1=H) and also di-t.butyl disulfide which are readily separated by chromatography. Using the same procedure but at reflux (v), four ketones 5 have been prepared. For the synthesis of the α,β-unsaturated β-silyl ketones , the vinyl ethers (4, $R^2=(CH_3)_3Si$) were (vi) first hydrolysed with dilute mineral acid to afford the β-t.butylthio β-trimethylsilyl ketones which are then treated with chloramine T [11].

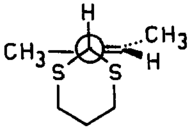
In conclusion, the carbanions 3 may be viewed as new equivalents of the β-acyl vinyl anions I [12].

REFERENCES AND NOTES

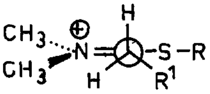
1. C. Bibang Bi Ekogha, O. Ruel, S.A. Julia, preceding communication.
2. All new compounds exhibited the expected IR, NMR (^1H, ^{13}C) and Mass spectral properties.

3. For a clear and concise presentation, the formulae of our substrates have been drawn directly in the favored conformations which allowed the protophilic attack by the base. Such overlap of the C-H bond with the olefin has recently been considered for the following substrates:

(a)



(b)



(a) F.E. Ziegler, J.-M. Fang, C.Ch. Tam, J. Amer. Chem. Soc., 104, 7174 (1982);
(b) Y. Tamaru, M. Mizutani, Y. Furukawa, O. Kitao, Z. Yoshida, Tetrahedron Letters, 23, 5319 (1982).

4. A mixture of the 3-methoxy-1-phenylthio-1-propenes (E/Z = ca 1:1) has been previously lithiated with LDA; after treatment with alkyl halides, predominant (Z) 1-alkylated isomers were obtained: M. Wada, H. Nakamura, T. Taguchi, H. Takei, Chem. Letters, 345 (1977).
5. Similar conditions have been reported to be the best for a rapid and efficient deprotonation of phenyl vinyl sulfide: H.J. Reich, W.W. Willis, Jr., J. Org. Chem., 45, 5227 (1980).
6. Such internally coordinated metallocycles have been invoked to represent the species formed by stereoselective lithiation of allylic ethers : W.C. Still, T.L. Macdonald, J. Amer. Chem. Soc., 96, 5561 (1974); J. Org. Chem., 41, 3620 (1976).
7. The E-compounds 2 undoubtedly result from nucleophilic reaction of methanol with the trans allylic equilibrated carbocation.
8. These regioselective alkylations are comparable to those of the 1-methylthio-3-triethylsilyloxy-pentadienyl lithium: W. Oppolzer, R.L. Snowden, P.H. Briner, Helv. Chim. Acta, 64, 2022 (1981).
9. Configurational assignments of the geometric isomers of 4 were readily made from:
   - the ^{1}H NMR spectra; the methoxy signals of the E-isomers are always shielded relative to those of the Z-isomers;
   - and from the relative ^{13}C chemical shifts values of the β-C atoms of the vinyl ethers: E. Taskinen, Tetrahedron, 34, 425 (1978); M.P. Strobel, C.G. Andrieu, D. Paquer, M. Vazeux, C.C. Pham, Nouveau J. Chim., 4, 101 (1980); D. Barillier, M.P. Strobel, L. Morin, D. Paquer, Tetrahedron, 39, 767 (1983).
10. K. Narasaka, T. Sakashita, T. Mukaiyama, Bull. Chem. Soc. Japan, 45, 3724 (1972).
11. The in situ formed N-tosylsulfimine [conditions of C.R. Johnson, K. Mori, A. Nakanishi, J. Org. Chem., 44, 2065 (1979)] underwent a facile cycloelimination with a β-H atom.
12. For other representative β-acylvinyl anions see: M. Julia, M. Badet, Bull. Soc. Chim. Fr., 1363 (1975); K. Kondo, D. Tunemoto, Tetrahedron Letters, 1007, 1397 (1975); J.C. Clinet, G. Linstrumelle, ibid., 1137 (1978) and the references cited therein.

(Received in France 17 July 1983)